

- AIR RESOURCES BOARD

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MEMORANDUM

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FROM: *Genevieve Shiroma*
Genevieve Shiroma
Chief, Toxic Air Contaminant Identification Branch

DATE: May 25, 1994

SUBJECT: AIR RESOURCES BOARD MONITORING OF METHIDATHION

In response to a Department of Pesticide Regulation (DPR) request, the Air Resources Board (ARB) staff conducted ambient and application site air monitoring in Tulare County for methidathion, and its oxidation product methidaoxon. The monitoring results and additional background information are included in the enclosures to this memorandum. A chronology of these events is Enclosure I. The complete results of the ambient and application site monitoring are included in Enclosure II.

If you have questions regarding this submittal, please contact me at (916) 322-7072.

Enclosures

John Sanders, Ph.D.

May 25, 1994

Page Two

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Enclosure I

Chronology of Events

**Methidathion Monitoring
Chronology of Major Events**

February 1991	DPR transmits to ARB monitoring recommendations for methidathion.
June 1991	ARB prepares draft work plan for methidathion sampling and analysis in Tulare County.
June 1991	ARB staff discusses methidathion use and sampling locations with representative of Tulare County Agricultural Commissioner's Office.
June 27 - July 25, 1991	Ambient monitoring is conducted at Tulare County sites.
July 10 - 13, 1991	Application site monitoring is conducted near an application to an orange orchard near Exeter.

May 23,

1991 - 1992

Enclosure II

Report on Ambient Concentrations of Methidathion
in Tulare County

Airborne Concentrations of Methidathion and Methidaoxon in Central Tulare County from Sampling Conducted in June and July 1991

**Prepared for California Air Resources Board
Contract No: A032-094**

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JUNE 24, 1993

**ENGINEERING
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DISCLAIMER

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ACKNOWLEDGEMENTS

The study presented in this report was supported by contract funds under ARB Research Contract No. A032-094, Monitoring Pesticides in Air. The authors of this report desire to acknowledge the valuable assistance provided by the staff of the Air Resources Board, particularly Lynn Baker, Ruth Tomlin, Ralph Propper, and Don Fitzell. We also thank personnel of the Tulare County Agriculture Commissioner's Office for the valuable information provided to us regarding pesticide application.

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Summary

The monitoring conducted in this study has been carried out at the request of the Department of Pesticide Regulation in support of their Toxic Air Contaminant Program. Both ambient and application monitoring for methidathion and its oxidation product, methidaoxon, were performed in Tulare County during June and July of 1991. Both methidathion and methidaoxon were detected at all five ambient monitoring sites and during the application monitoring period. Table 1 contains a summary of the findings. Appendices A, B and C contain a more detailed presentation of the monitoring data.

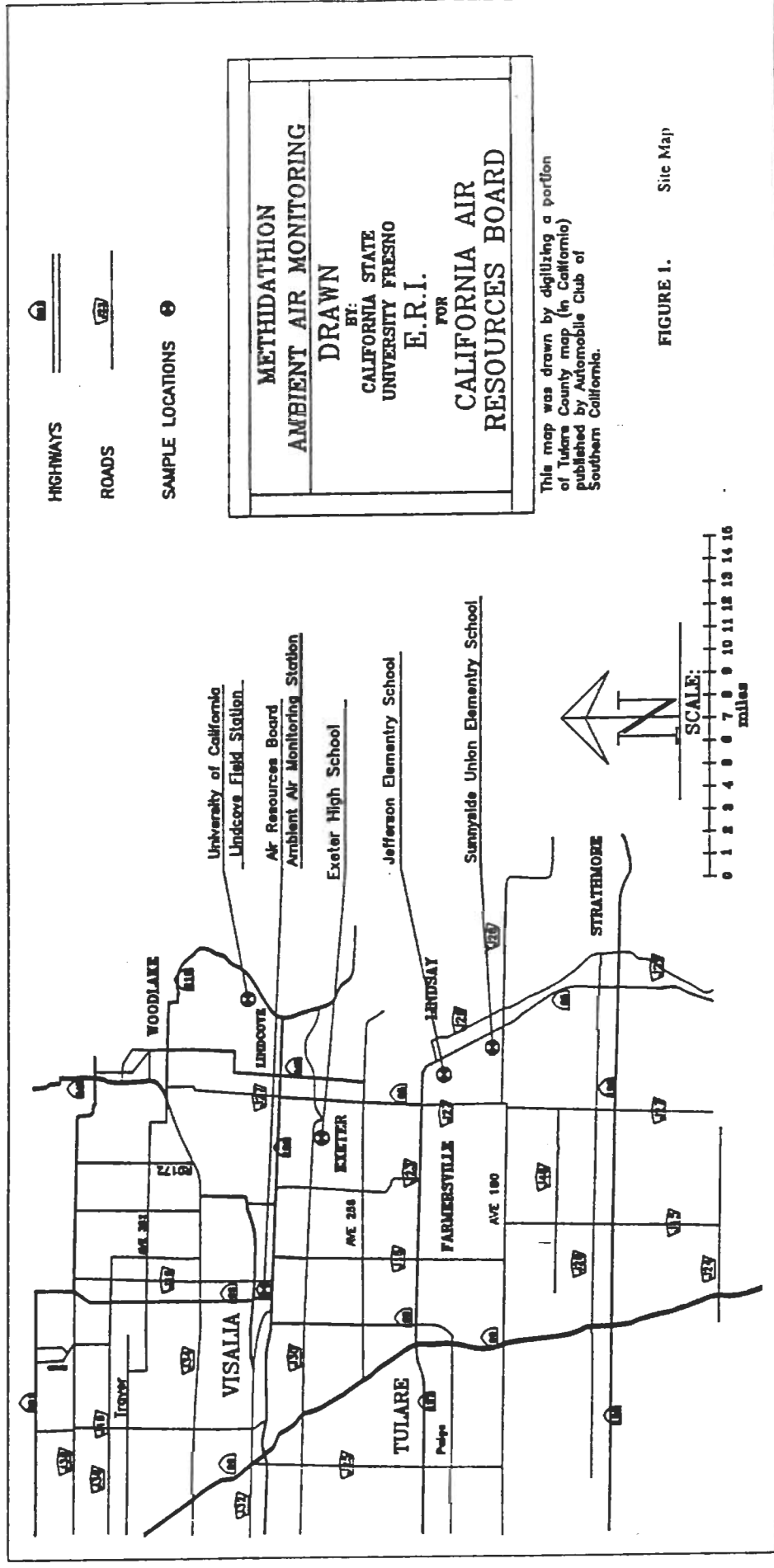
Table 1. Summary of Methidathion Results					
Site	Highest Value	Second Highest Value	Mean of Results > LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	<LOQ	<LOQ	—	0	17
Jefferson Elementary School	0.56	0.30	0.16	6	17
Exeter Union High School	0.070	<LOQ	0.070	1	15
UC Lindcove Field Station	<LOQ	<LOQ	—	0	15
ARB Monitoring Station, Visalia	<LOQ	<LOQ	—	0	17

NOTE: LOQ for methidathion is 0.03 $\mu\text{g}/\text{m}^3$

Table 2. Summary of Methidaoxon Results					
Site	Highest Value	Second Highest Value	Mean of Results > LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	.092	<LOQ	.092	1	17
Jefferson Elementary School	0.10	<LOQ	0.10	1	17
Exeter Union High School	<LOQ	<LOQ	—	0	15
UC Lindcove Field Station	<LOQ	<LOQ	—	0	15
ARB Monitoring Station, Visalia	<LOQ	<LOQ	—	0	17

NOTE: LOQ for methidaoxon is 0.09 $\mu\text{g}/\text{m}^3$

Detectable level of methidathion were found during all application monitoring sampling periods except the initial background period, while methidaoxon was found only during the last three sampling periods. The peak concentrations were found in samples 5N ($3.16 \mu\text{g}/\text{m}^3$) and 4SW1 ($0.36 \mu\text{g}/\text{m}^3$) for methidathion and methidaoxon, respectively.



INTRODUCTION

Very low flow volume (4 *lpm*) ambient air samples were collected at five sites (including background site) in Tulare County for analysis of an organophosphate insecticide, methidathion (*O, O*-dimethyl phosphorodithioate *S*-ester with 4(mercaptomethyl)-2-methoxy- δ -2-1,3,4-thiadiazolin-5-one), a restricted use pesticide which is the active ingredient in a product formulated as an emulsifiable concentrate. The location and time period for sampling were based on reported applications of methidathion in recent years. Tulare County was selected as the study area since within California it had a history of having the largest applications of methidathion (70,532 pounds active ingredient in 1988). Typically, peak usage in Tulare County occurs in the June-July period when methidathion is applied to orange trees, the principal use of this insecticide. Other crops to which methidathion is also applied in large quantities include almonds, alfalfa, cotton, and artichokes.

SITE DESCRIPTION

Five sampling sites were chosen by California Air Resources Board (ARB) personnel from an area of Tulare County where orange orchards are predominant. With the exception of the ARB Monitoring Station, the sampling sites selected are within the citrus fruit production area of Tulare County. These sites have citrus groves within one-quarter miles of their boundaries in which methidathion application were expected. Site selection criteria also included considerations for both accessibility and security of the sampling equipment. The five selected sites were the following locations: Sunnyside Union Elementary School, Strathmore; Jefferson Elementary School, Lindsay; Exeter Union High School, Exeter; the University of California (UC) Lindcove Field Station, Exeter; and the ARB Ambient Air Monitoring Station, Visalia (Figure 1). The latter site was the site used for monitoring background concentration. Samplers were located on the roof of a building at each site except at the Lindcove Field Station. The Lindcove Field Station is a citrus study facility and the sampler was positioned in an open area near the meteorological station located on-site. Both elementary schools are located within one-quarter mile of orange orchards. The orange groves nearest to Exeter Union High School are located one-quarter mile north of the school. No orange groves are in existence near the City of Visalia where the background monitoring site was set up.

The samples were collected by California State University, Fresno (CSUF) personnel over a four week period from June 27 - July 25, 1991. Samples were transported to CSUF for analysis.

SAMPLING

Ambient samplers consisted of a glass tube (8mm x 110mm) containing two sections of XAD-2 resin (400 mg primary section with 200 mg backup section) connected by Teflon tubing to a

flowmeter and a sampling pump. Each sampling pump had two resin tubes attached to it with the air flow through each tube being monitored by an independent flowmeter. A diagram of the sampling apparatus is presented in Figure 2. Flow rates for each sampling tube were measured at the beginning and at the end of each sampling period. Sampling periods were nominally 24 hours and varied from approximately 23 to 25 hours. The sampling data are presented in Appendix A. At the end of the sampling period, each resin tube was removed from the sampling apparatus and capped, labeled, and placed in a screw cap glass culture tube. The culture tubes with their contents were then placed on ice in an ice chest. The samples were stored in the ice chests until delivery at the end of each sampling day to CSUF for analysis. At CSUF samples were stored in a freezer at -15°C until extracted for analysis.

Application monitoring was conducted by the ARB Evaluation Branch during the month of July. The report for this monitoring is at Appendix B.

LABORATORY ANALYSIS

All samples for ambient and application monitoring were prepared for analysis within seven days of sampling. All samples were warmed to room temperature before extraction. The primary section of resin in each sample was extracted in 2.0 mL of toluene by sonicating for 30 minutes. The backup section of the resin was not extracted based upon breakthrough studies conducted during the method evaluation. No breakthrough was demonstrated for either compound at levels up to 100 μg . The extract was allowed to settle, filtered through a plug of glass wool, and transferred to a 4 mL vial for gas chromatographic analysis. No additional cleanup was required.

The samples were analyzed on a Varian 3400 gas chromatograph equipped with a Ni^{63} electron capture detector and a Varian model 4290 integrator. A J&W Scientific DB-5 megabore column (30m x 0.53mm ID) provided the separation. The table below contains the instrument conditions.

Table 3. Instrument Conditions								
Temperatures		Column Program					Gas Flows (mL/min)	
Injector °C	Detector °C	Initial °C	Hold min	Ramp °C/min	Final °C	Hold min	Carrier N ₂	Make Up N ₂
220	280	200	1	10	250	6	8	22

PESTICIDE SAMPLING APPARATUS

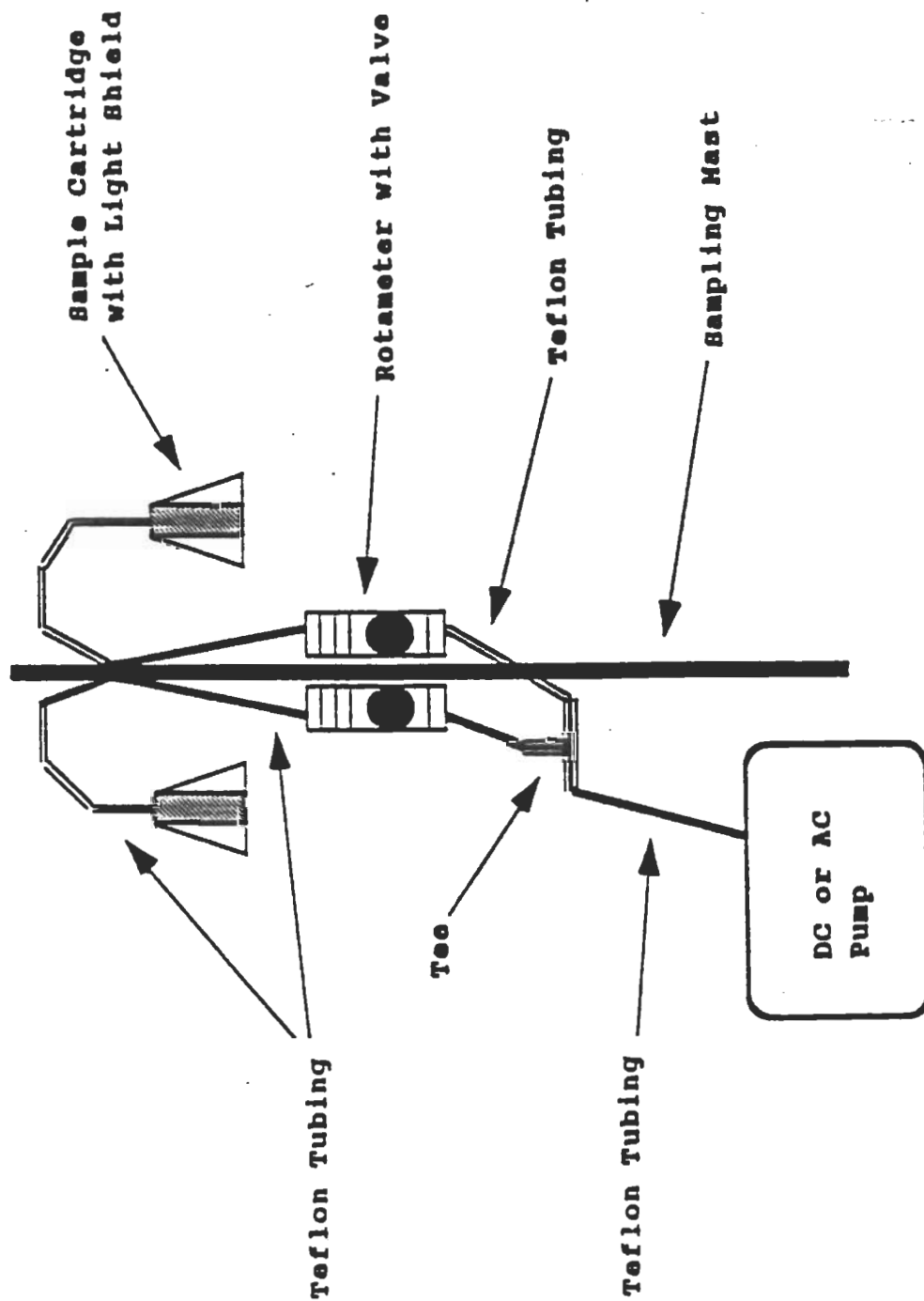


Figure 2 SAMPLING APPARATUS

A four point calibration curve was prepared by injecting 2 μL of each of the working standards into the gas chromatograph. A second-order equation for the standard curve was generated from the resulting peak area data using Cricket Graph™. Two microliters of each sample were injected into the gas chromatograph for comparison to the standards.

The analytical results for methidaoxon and methidathion are found in Appendix C at the end of this report.

An example using the chromatograms and equations for one set of standard curves can be found in Appendix D.

QUALITY CONTROL/QUALITY ASSURANCE

Sampling and analysis were conducted according to the project quality assurance plan. Collocated replicate samples were collected at each sampling site for each sampling period. Replicate samples from one site each week (20% of the samples) were analyzed as part of the quality control requirements. In addition, control spikes were analyzed with each extraction set to monitor extraction efficiencies. When detectable levels of the study compound were identified, the replicate sample was also extracted and analyzed.

The limit of detection (LOD) was determined to be three times the standard deviation of replicate injections of the lowest standard. The limit of quantitation (LOQ) is three times the LOD. The limit of detection (LOD) for methidathion and its oxidation product, methidaoxon, in air are 0.01 and 0.03 $\mu\text{g}/\text{m}^3$, respectively. The LOQ is 0.03 and 0.09 $\mu\text{g}/\text{m}^3$ for methidathion and methidaoxon, respectively.

A set of control samples was prepared and submitted to CSUF by Gabriel Ruiz (ARB) during the monitoring period. These were analyzed and the data returned to ARB for analysis and a separate report was prepared by Gabriel Ruiz (Appendix E).

During the method validation, a number of parameters were evaluated. The parameters studied include extraction efficiency, sampling recovery, and storage stability. The data for these parameters are presented in Appendix F.

During the retention efficiency studies, a low-level background for methidaoxon was identified. This background was also found in the field blanks. The average background value for the retention blanks, the samples of the backup section of the breakthrough studies, and the field blanks is $0.13 \pm 0.02 \mu\text{g}$ of methidaoxon. This corresponds to a concentration of $0.023 \mu\text{g}/\text{m}^3$. The background appears to be an artifact of the sampling process. It may be either a low-level material extracted from the XAD-2 resin or possibly an interfering substance in the ambient air.

RESULTS AND DISCUSSION

Figures 3-1 and 3-2 through figures 7-1 and 7-2 show methidaoxon and methidathion data, respectively, as a function of the day of the study for the five study sites. The methidaoxon and methidathion data for the Sunnyside Union Elementary School site are shown in figures 8-1 and 8-2, respectively, as a function of the probability of occurrence (a statistical measure of the probability the concentration of the pesticide in the sample equalled or exceeded a selected concentration given that the sample population is normally distributed). Likewise, the methidaoxon and methidathion data for the Jefferson Elementary School site are shown in figures 9-1 and 9-2, respectively, as a function of the probability of occurrence. The plotted data are not blank corrected (0.024 and $0.001 \mu\text{g}/\text{m}^3$ for methidaoxon and methidathion, respectively).

The five sampling sites, including the intended background site (the Air Resources Board Monitoring Station in Visalia) had positive results for methidathion and its oxidation product, methidaoxon, during part of the ambient monitoring period. Results ranged from below the LOD to a high of $0.56 \mu\text{g}/\text{m}^3$ for methidathion at the Jefferson Elementary School site (figure 4-2), and a high of $0.12 \mu\text{g}/\text{m}^3$ for methidaoxon at the Exeter Union High School site (figure 5-1).

Both methidaoxon and methidathion were consistently detected at the Sunnyside Union Elementary School site (figures 3-1 and 3-2) above the LOD with maximum values detected being 0.092 and $0.029 \mu\text{g}/\text{m}^3$, respectively.

The most extreme values for methidathion in air occurred at the Jefferson Elementary School site (figure 4-2). Of particular note is the two week period of July 10-23, 1992 (study days 15-27). During this period the methidathion concentration peaked at $0.56 \mu\text{g}/\text{m}^3$ and averaged $0.13 \mu\text{g}/\text{m}^3$. The methidaoxon concentration at this site during the early part of this time period was also elevated having a peak concentration of $0.11 \mu\text{g}/\text{m}^3$ on July 10, 1991 (study day 15). However, another high methidaoxon concentration at the Jefferson Elementary School site occurred on July 2, 1991 (study day 6) and no apparent increase of methidathion, the precursor compound, is noted.

The remainder of the data shown on figures 5-1, 5-2, 6-1, 6-2, 7-1, and 7-2 are generally near the LOD. A correlation does not appear to exist for the occurrence of detectable quantities of methidaoxon as a function of detectable quantities of methidathion. An investigation of this must include consideration of particle transport in air, meteorological conditions, and the ambient oxidation rates of methidathion.

The fact that methidaoxon and methidathion were detected eight and two times, respectively, at the Air Resource Board Monitoring Station in Visalia (figures 7-1 and 7-2) is significant since this site is located in a downtown area and not in the immediate area of a known use of methidathion (the County Agricultural Commissioner has stated that no known applications of methidathion occurred in the immediate area of downtown Visalia during this time period). These compounds appear to persist sufficiently long to be transported into populated areas from the region in which the application takes place.

Figures 3-1, 4-1, 5-1, and 7-1 show relatively high concentrations of methidaoxon for July 25, 1991 (study day 29). The samples from which these data were determined were analyzed together with standards, external quality assurance samples, control samples, and samples from application monitoring and day 28 ambient monitoring. After reviewing these data the results are deemed to be valid.

In the preparation of the data for figures 8-1, 8-2, 9-1, and 9-2, all the data including the data points for data below the LOD were used to calculate the probability interval. An evaluation of these figures show the data to be generally normally distributed. Significant outliers are found with the Jefferson Elementary School data (figures 9-1 and 9-2) for the few very high data points. These data are significantly above the LOQ's for methidaoxon and methidathion, respectively, and they have a low probability of occurrence.

CONCLUSIONS

All data presented in this report for methidaoxon and methidathion have been determined and accepted subject to a rigorous quality assurance program. Most data are below, at, or slightly above the LOD's for both methidaoxon and methidathion, and few data were above the LOQ's for these compounds.

Methidaoxon and methidathion can persist for extended periods of time at elevated concentrations at sites near where application of an insecticide having methidathion as the active ingredient is being carried out. The persistence of these compounds may be responsible for their detection at the Air Resources Board Monitoring Station site which is located in an urban area and not in the immediate locale of known application of methidathion.

METHIDAOXON CONCENTRATION DATA FOR SUNNYSIDE UNION ELEMENTARY SCHOOL SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.015 ug/cu. m).

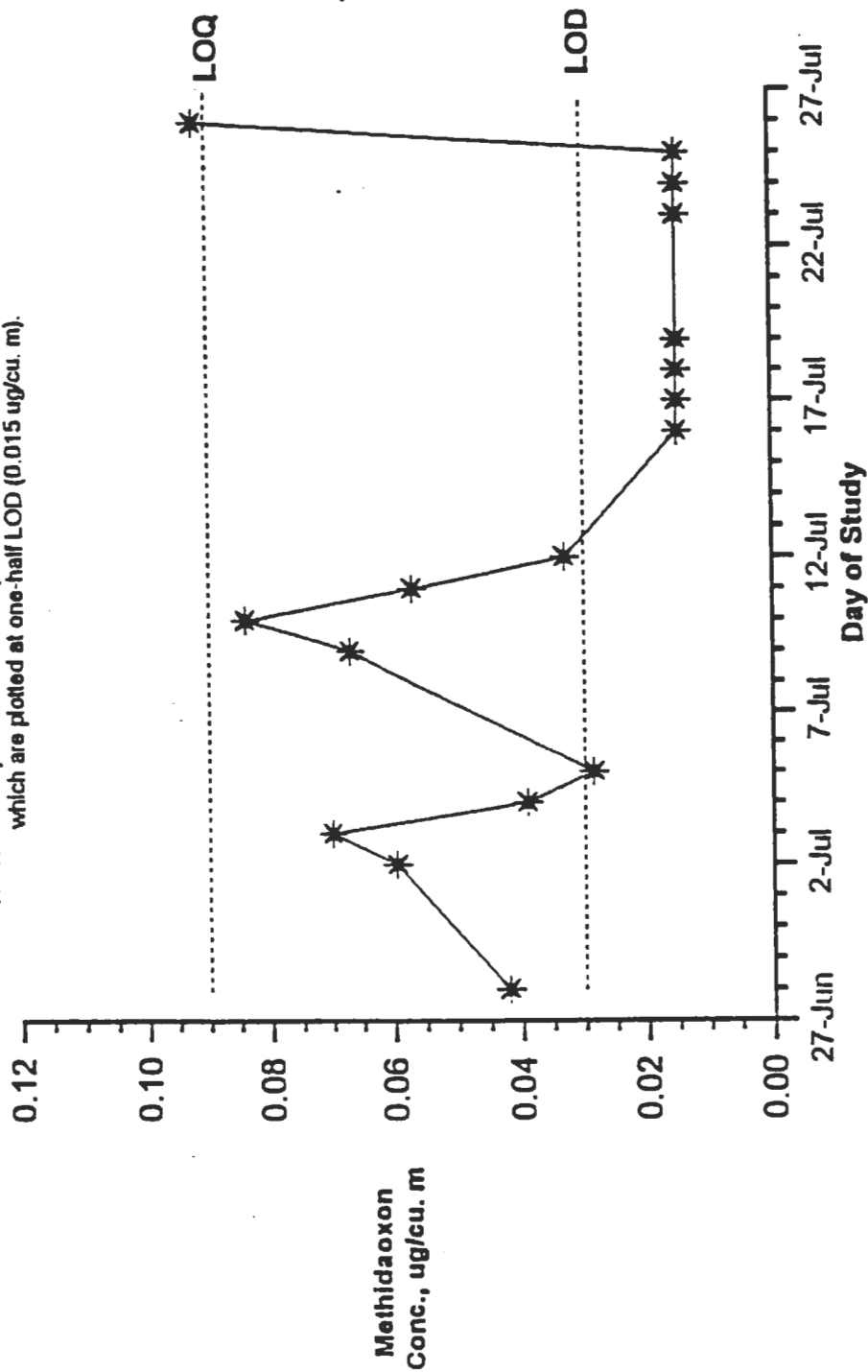


Fig. 3-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Sunnyside Union Elementary School site during the June 27 - July 25, 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR SUNNYSIDE UNION ELEMENTARY SCHOOL SITE

NOTE: Data points on x-axis represent nondetectable (ND) results
which are plotted at one-half LOD (0.005 ug/cu. m).

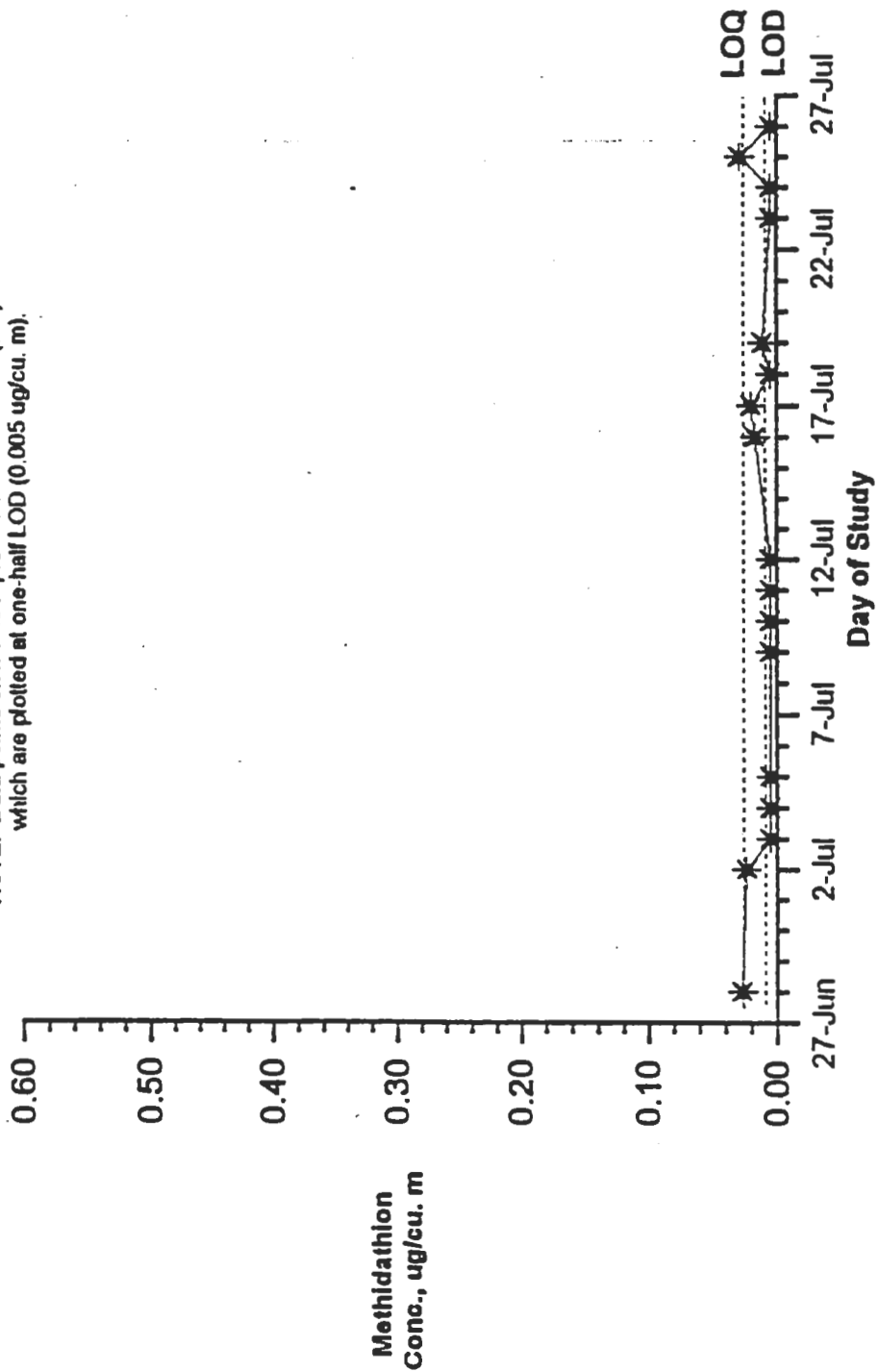


Fig. 3-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Sunnyside Union Elementary School site during the June 27 - July 25, 1991 sampling period.

METHIDAOXON CONCENTRATION DATA FOR JEFERSON ELEMENTARY SCHOOL SITE

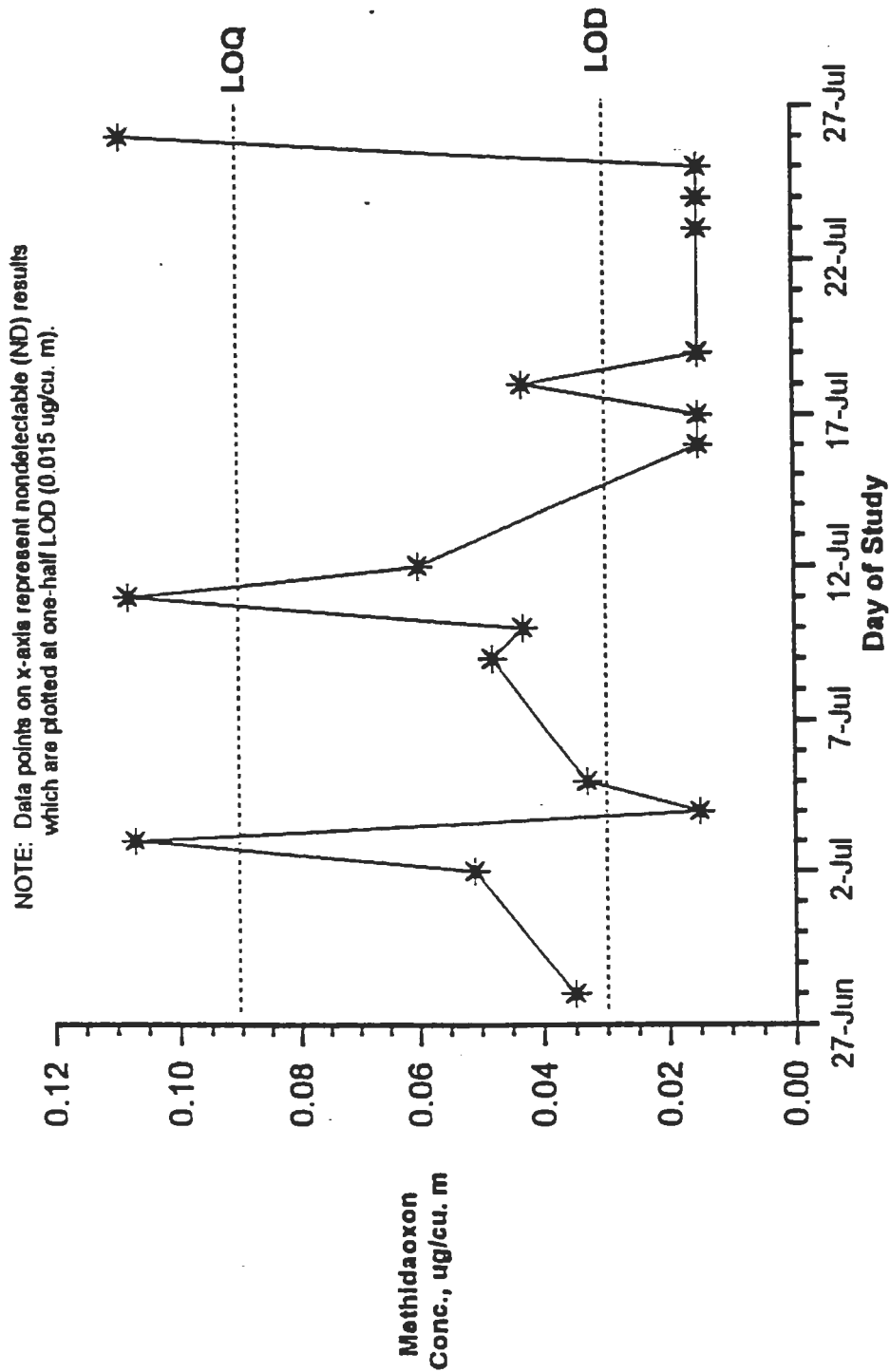


Fig. 4-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Jefferson Elementary School site during the June 27 - July 25, 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR JEFFERSON ELEMENTARY SCHOOL SITE

NOTE: Data points on x-axis represent nondetectable (ND) results
which are plotted at one-half LOD (0.005 ug/cu. m).

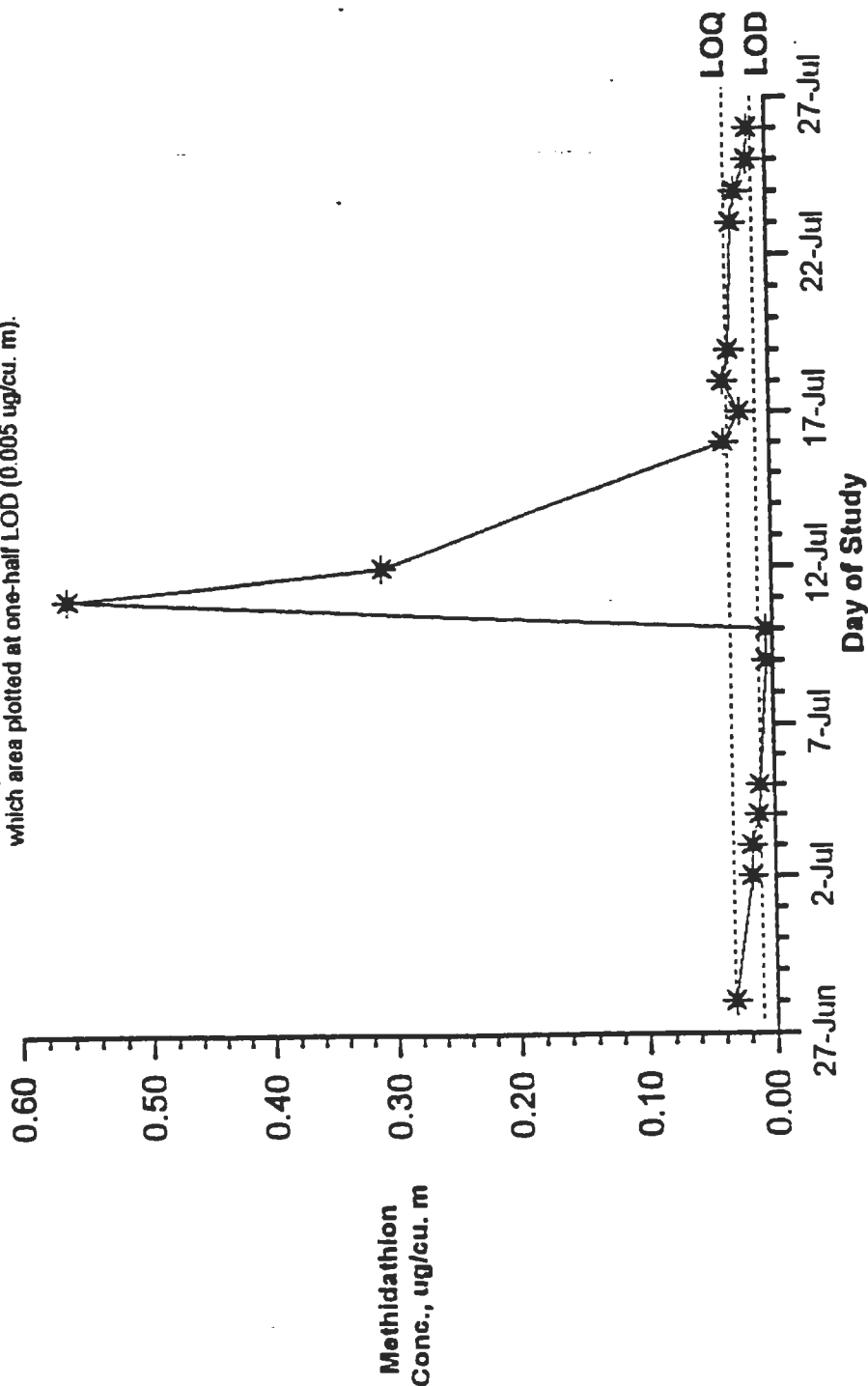


Fig. 4-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Jefferson Elementary School site during the June 27 - July 25, 1991 sampling period.

METHIDAOXON CONCENTRATION DATA FOR EXETER HIGH SCHOOL SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.015 ug/cu. m).

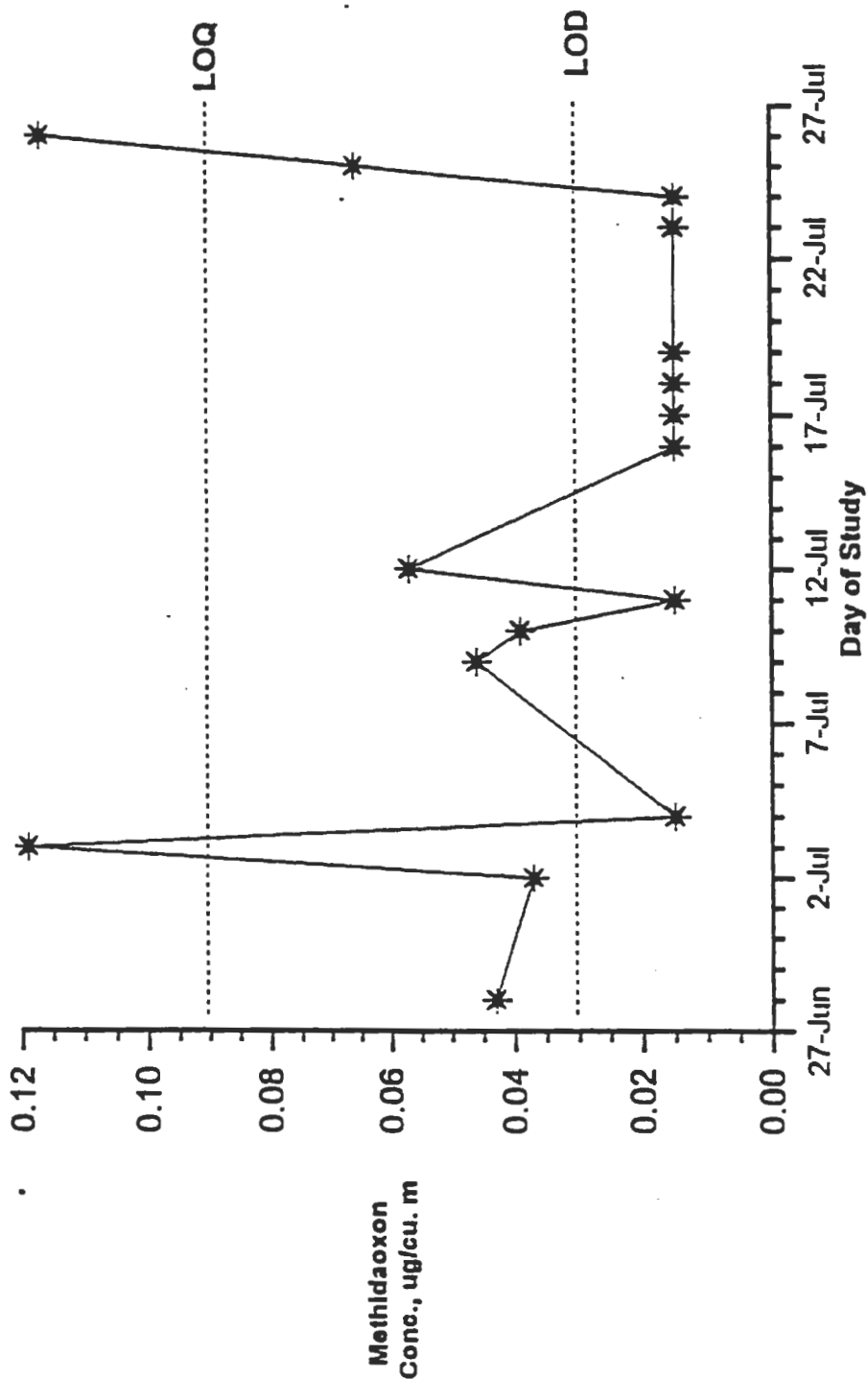


Fig. 5-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Exeter Union High School site during the June 27 - July 25, 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR EXETER UNION HIGH SCHOOL SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.005 ug/cu. m).

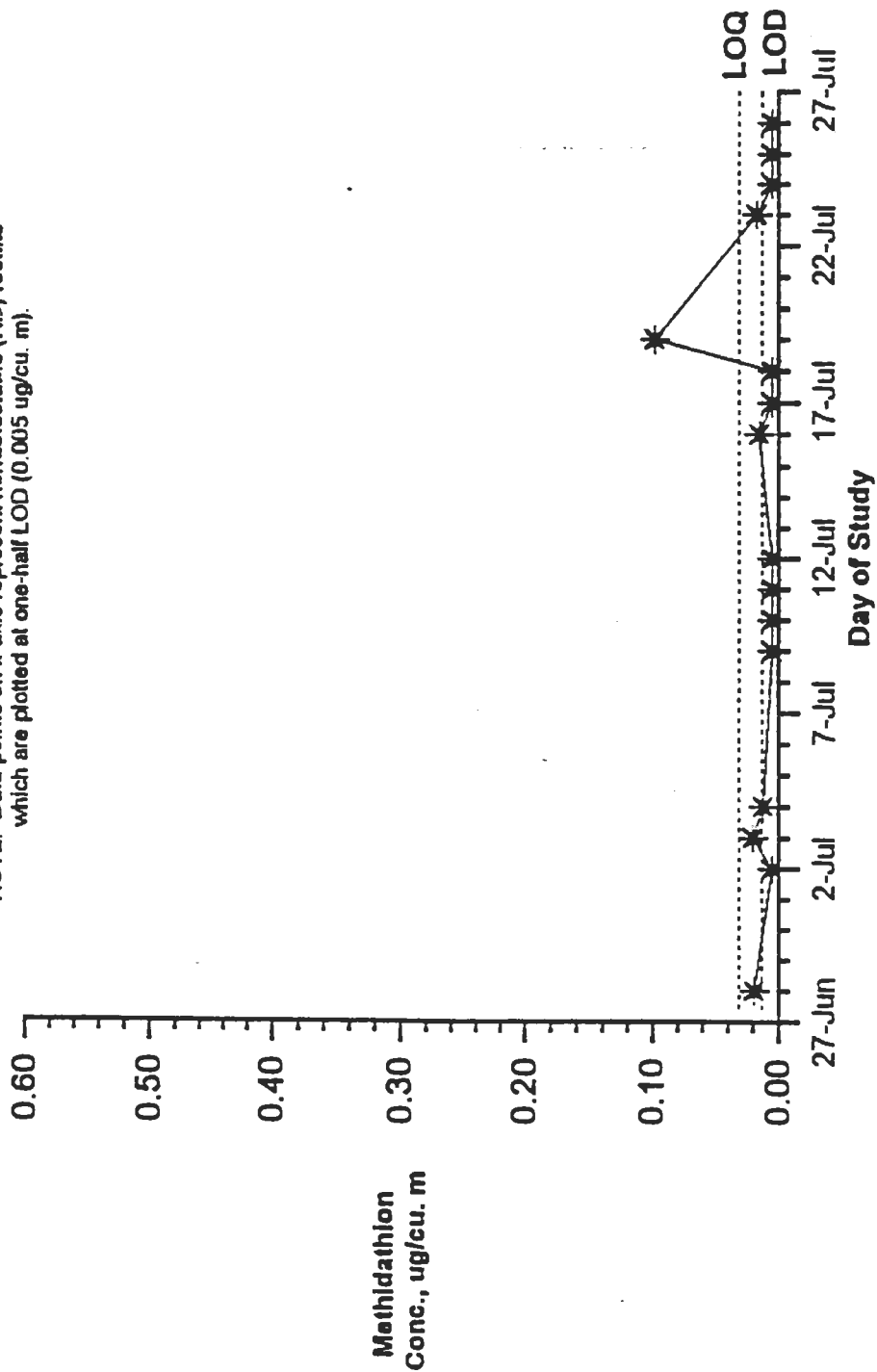


Fig. 5-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Exeter Union High School site during the June 27 - July 25, 1991 sampling period.

METHIDAOXON CONCENTRATION DATA FOR UC LINDCOVE FIELD STATION SITE

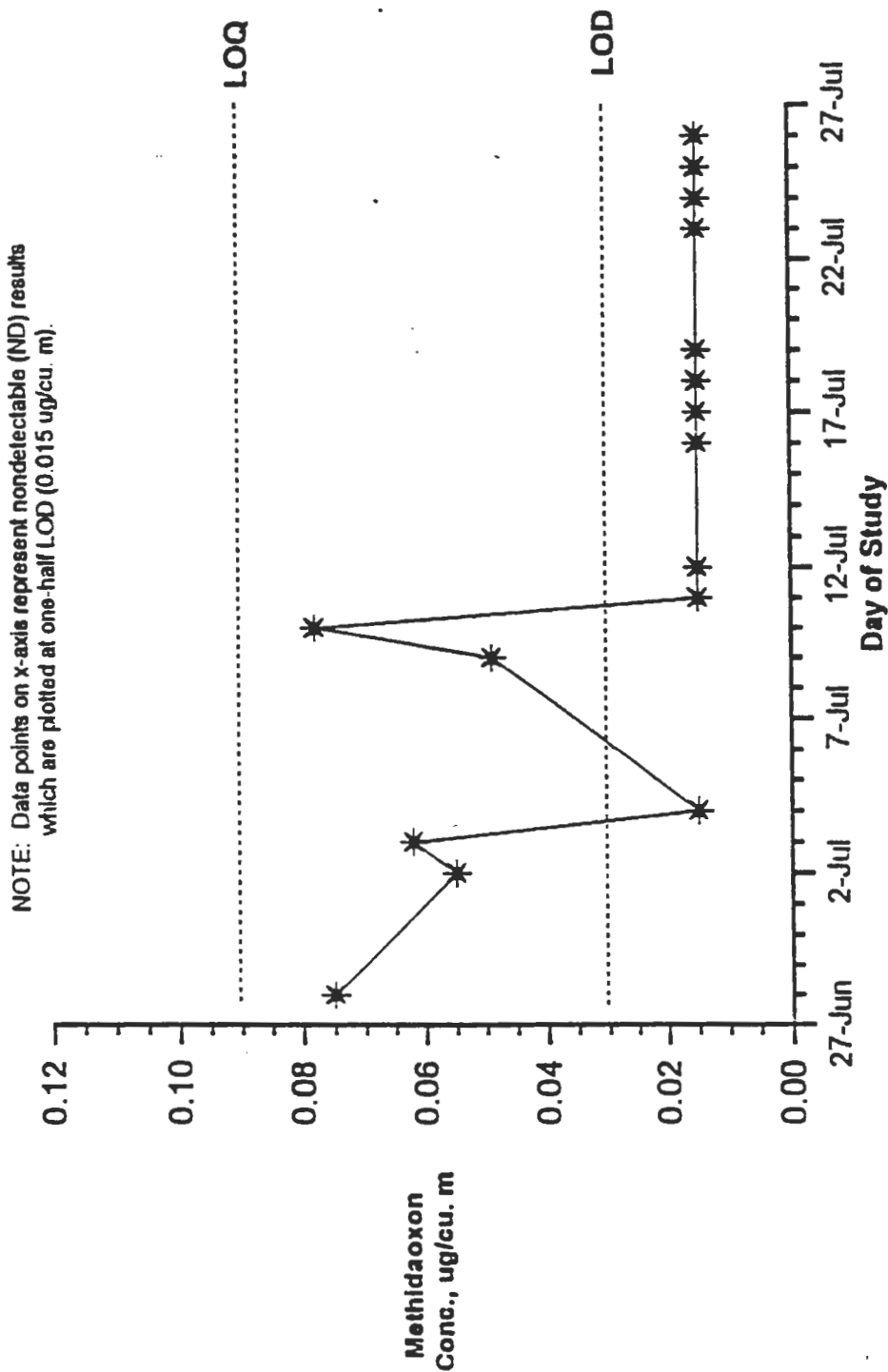


Fig. 6-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the UC Lindcove Field Station site during the June 27 - July 25, 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR UC LINDCOVE FIELD STATION SITE

NOTE: Data points on x-axis represent nondetectable (ND) results
which are plotted at one-half LOD (0.005 ug/cu. m).

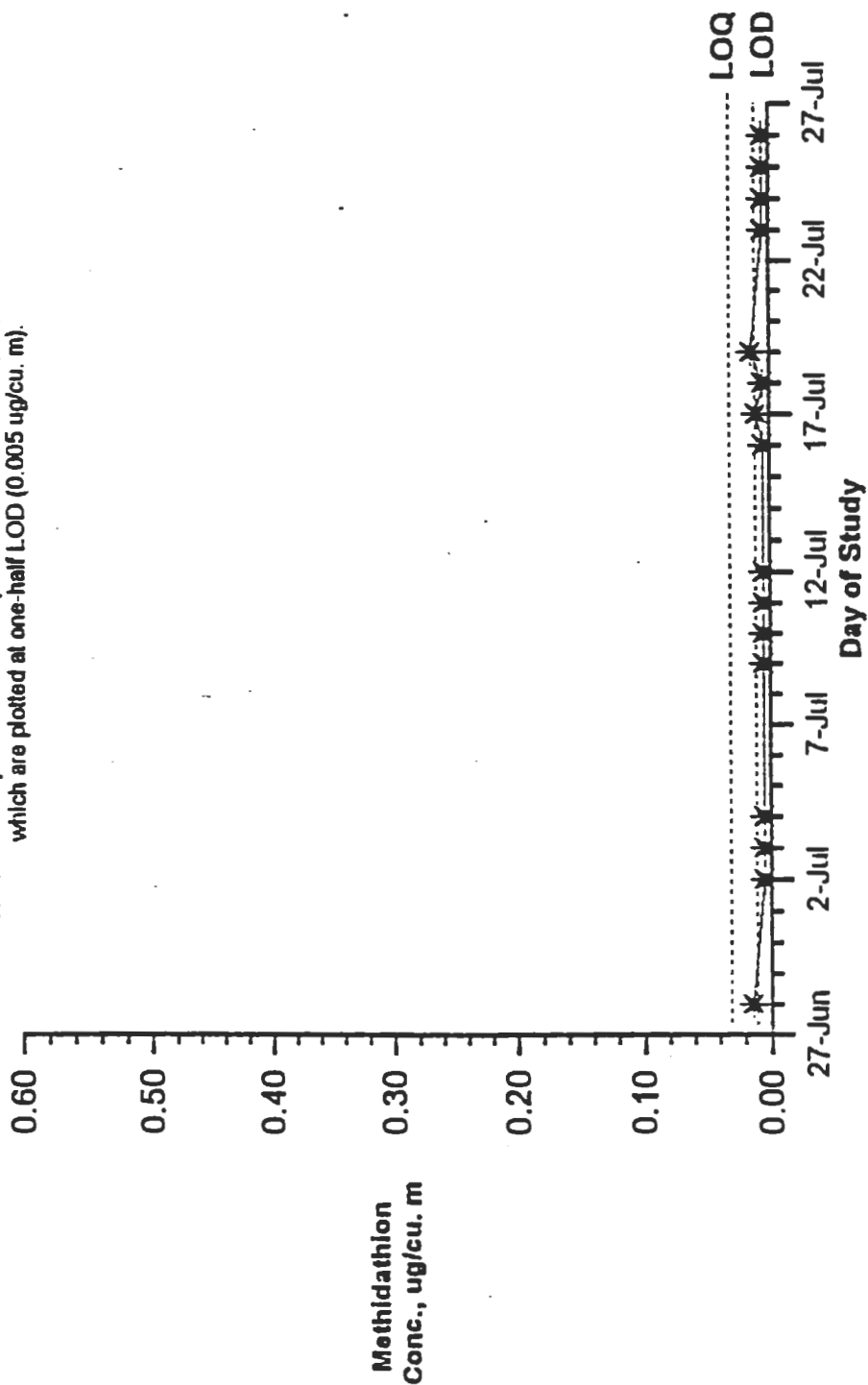


Fig. 6-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the UC Lindcove Field Station site during the June 27 - July 25, 1991 sampling period.

METHIDAOXON CONCENTRATION DATA FOR AIR RESOURCES BOARD MONITORING STATION SITE

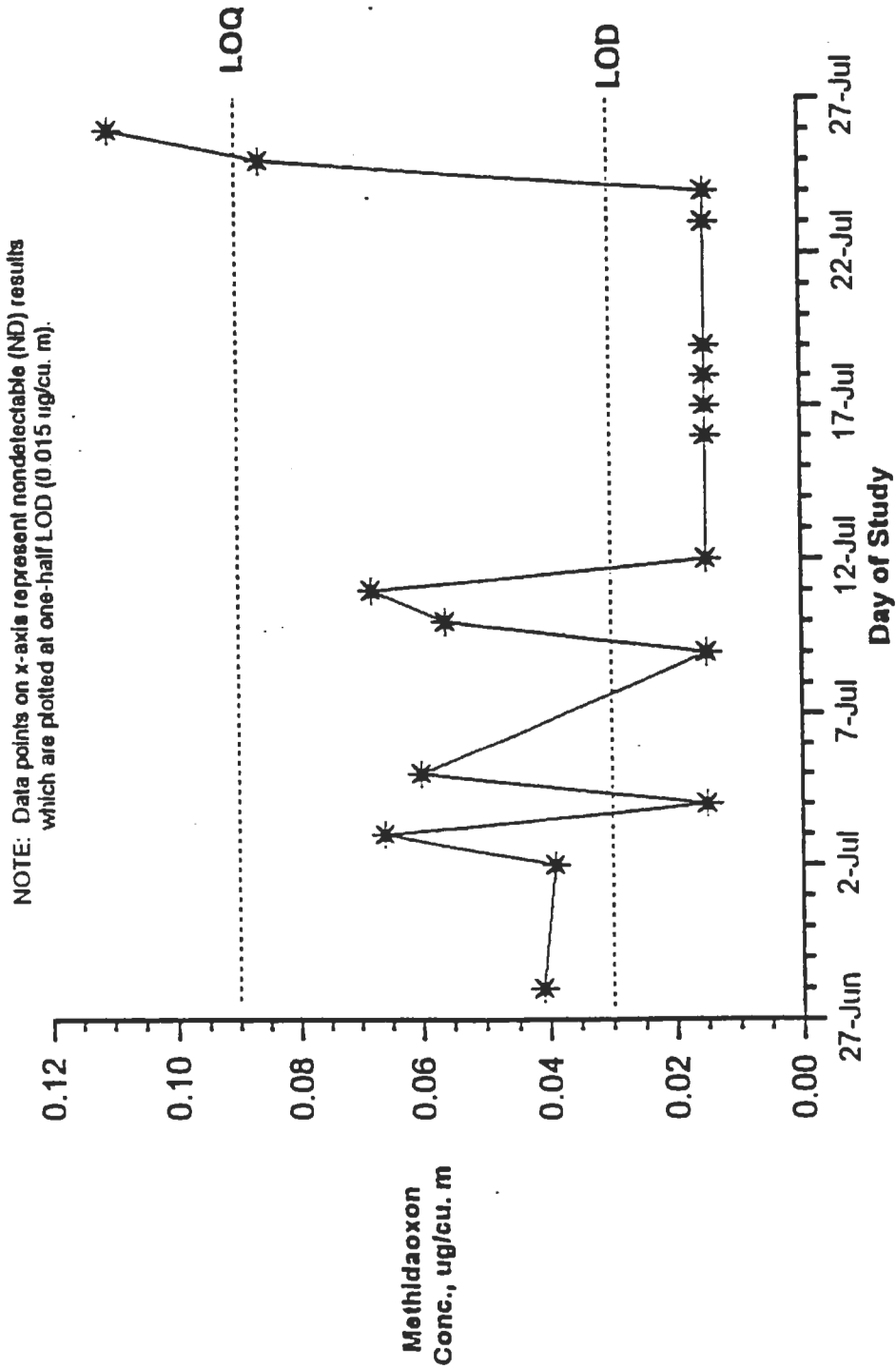


Fig. 7-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the ARB Monitoring Station site during the June 27 - July 25, 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR AIR RESOURCES BOARD MONITORING STATION SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.005 ug/cu. m).

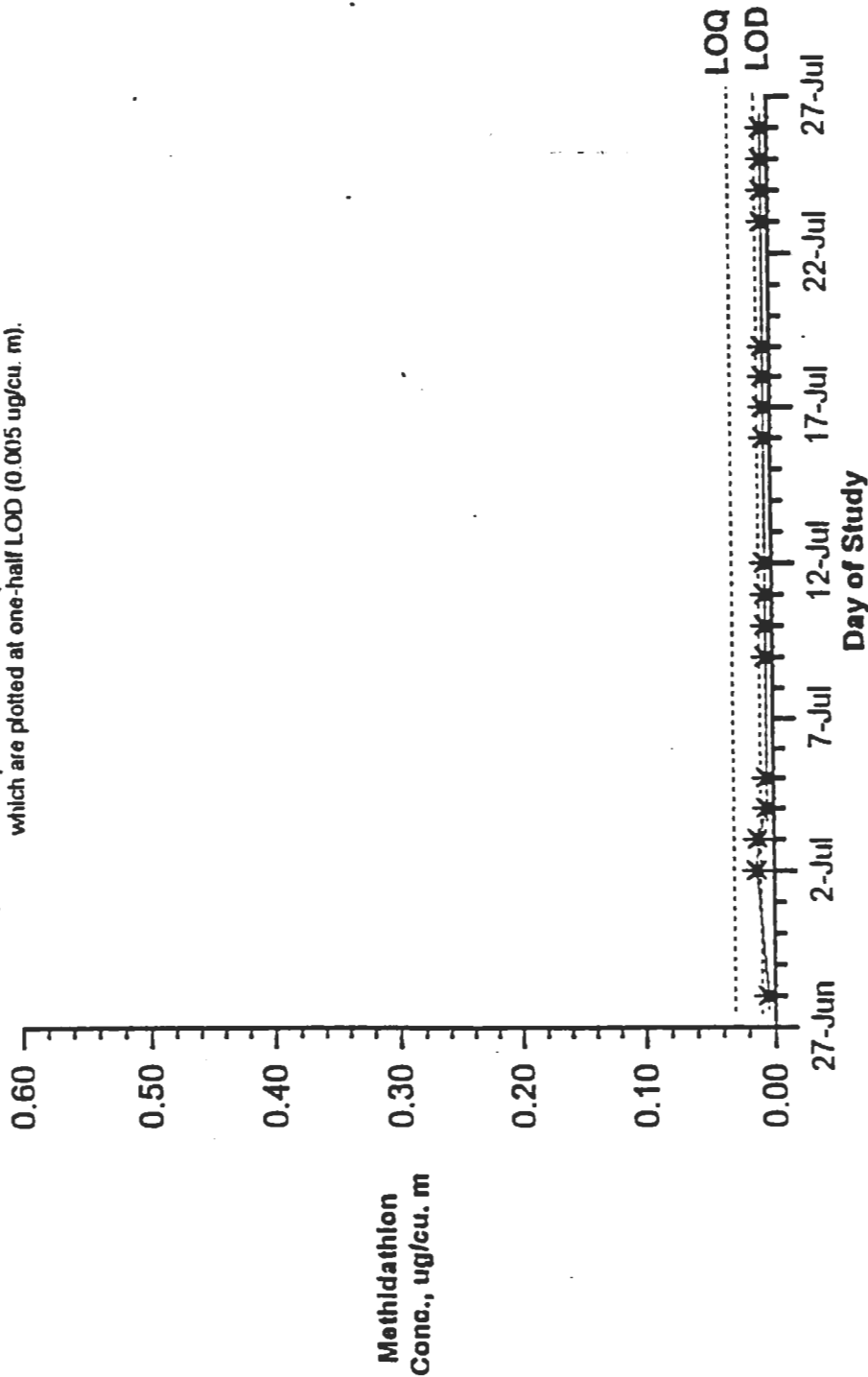


Fig. 7-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the ARB Monitoring Station site during the June 27 - July 25, 1991 sampling period.

METHIDAOXON CONCENTRATION DATA FOR SUNNYSIDE UNION ELEMENTARY SCHOOL SITE

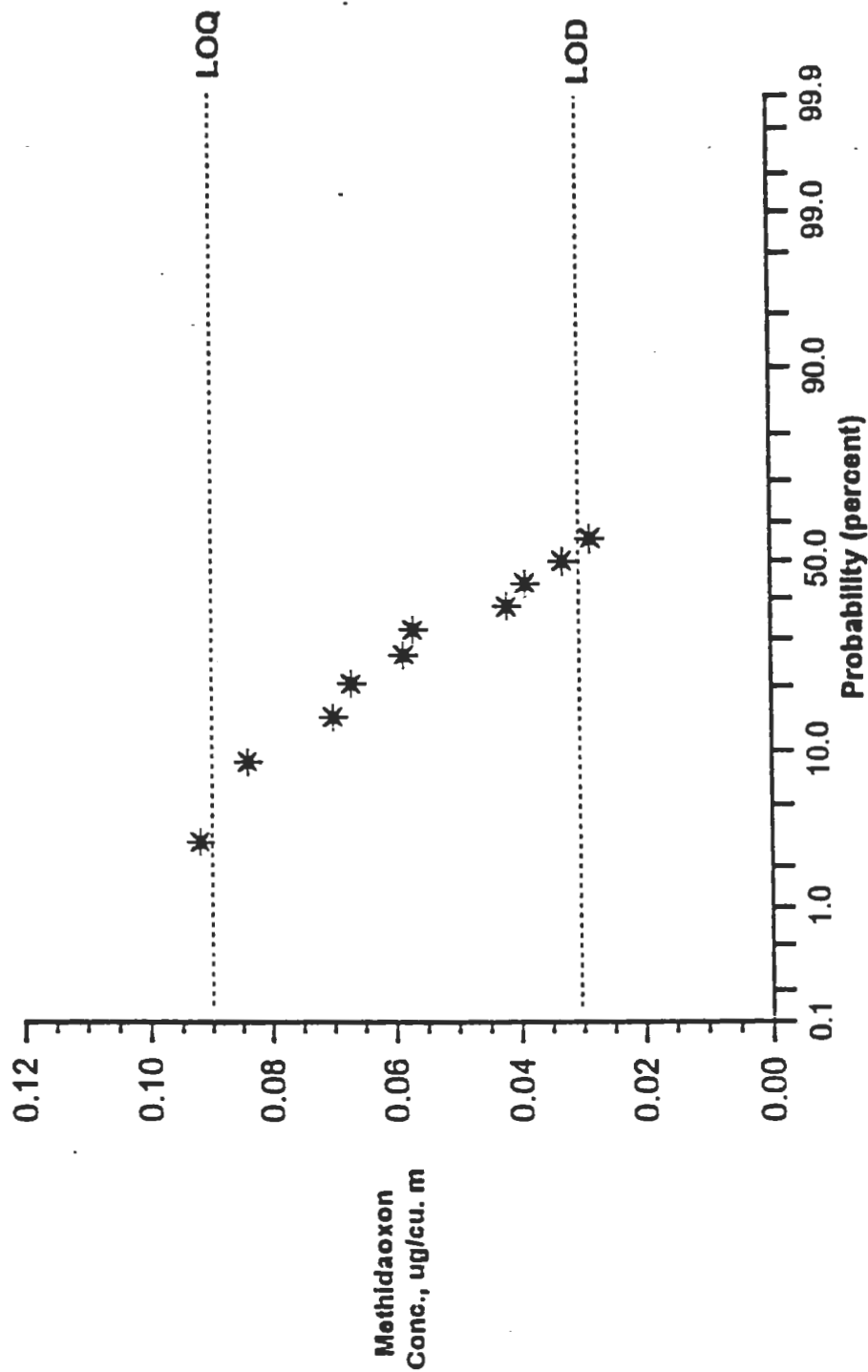


Fig. 8-1. Methidaoxon concentration in micrograms per cubic meter as function of probability (%) of methidaoxon concentration being equal to or greater than the plotted values at the Sunnyside Union Elementary School site during the June-July 1991 sampling period.

The figure is a scatter plot with the following characteristics:

- Y-axis:** Labeled "Methidathion Conc., ug/cu. m", ranging from 0.00 to 0.60 with major ticks every 0.10 and minor ticks every 0.02.
- X-axis:** Labeled "Probability (percent)", with a non-linear scale ranging from 0.1 to 99.9. Major ticks are at 0.1, 1.0, 10.0, 50.0, 90.0, 99.0, and 99.9.
- Data Points:** Represented by asterisks (*). There are 10 data points clustered between 1.0% and 10.0% probability, with concentrations ranging from approximately 0.02 to 0.05 ug/cu. m. No data points are visible at higher probabilities.
- Reference Lines:** Two horizontal dashed lines are present. The upper line is labeled "LOQ" (Limit of Quantitation) at approximately 0.04 ug/cu. m. The lower line is labeled "LOD" (Limit of Detection) at approximately 0.02 ug/cu. m.

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METHIDAOXON CONCENTRATION DATA FOR JEFFERSON ELEMENTARY SCHOOL SITE

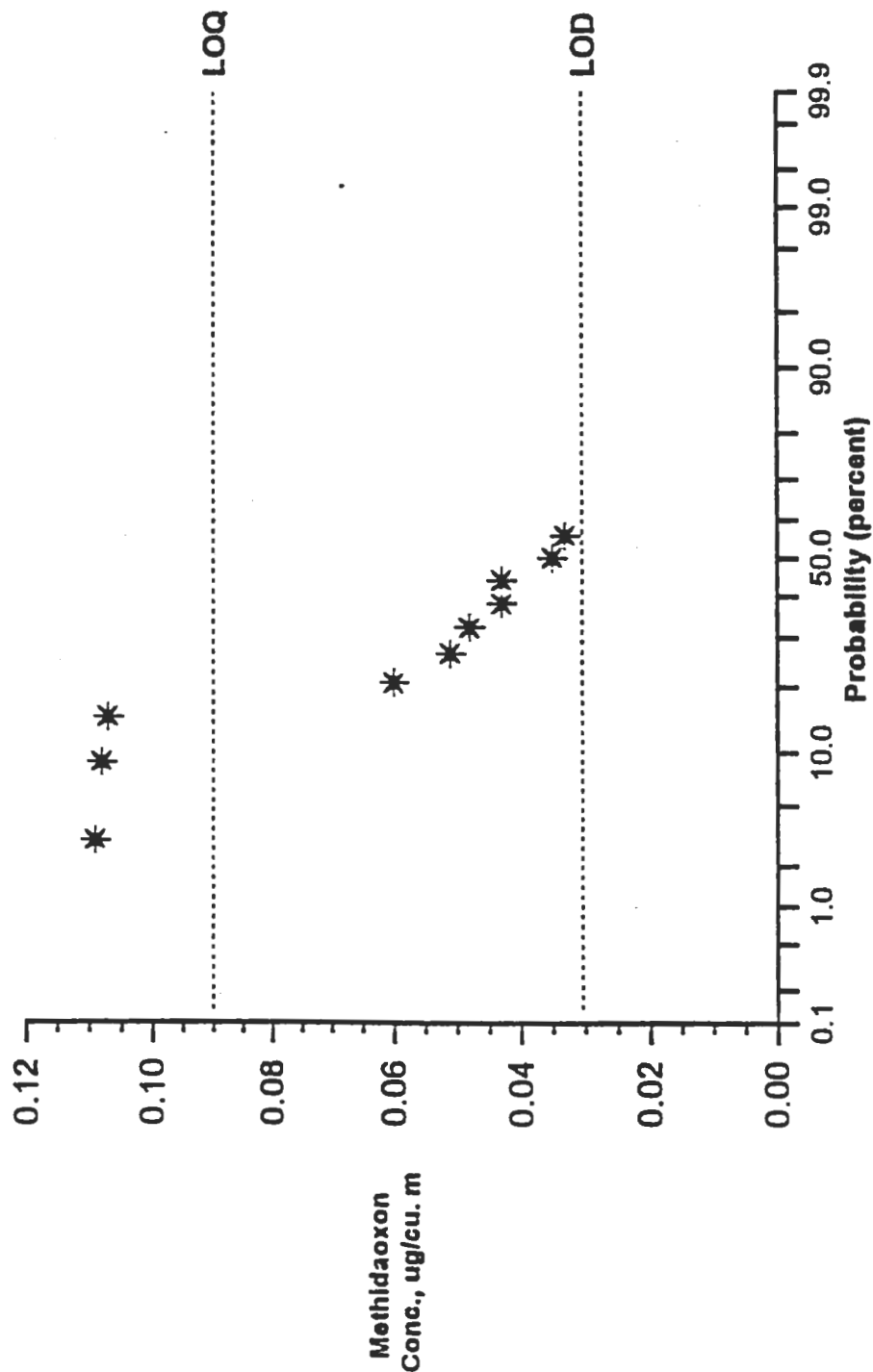


Fig. 9-1. Methidaoxon concentration in micrograms per cubic meter as function of probability (%) of methidaoxon concentration being equal to or greater than the plotted values at the Jefferson Elementary School site during the June-July 1991 sampling period.

METHIDATHION CONCENTRATION DATA FOR JEFFERSON ELEMENTARY SCHOOL SITE

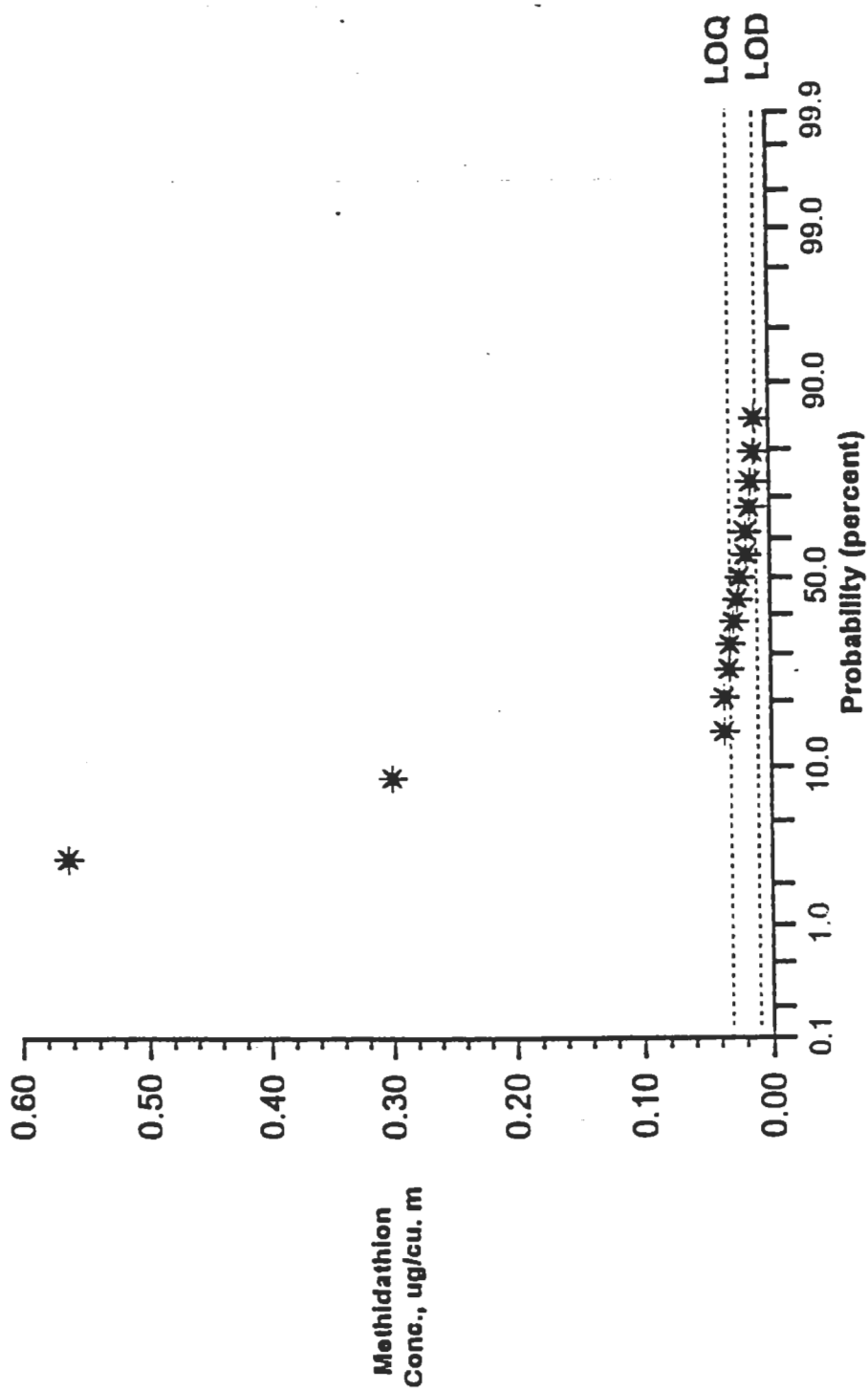


Fig. 9-2. Methidathion concentration in micrograms per cubic meter as function of probability (%) of methidathion concentration being equal to or greater than the plotted values at the Jefferson Elementary School site during the June-July 1991 sampling period.

APPENDIX A
SAMPLING DATA

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m ³)
0 S	27-Jun-91	11:25	28-Jun-91	11:00	23.6	3.9	5.519
0 J	27-Jun-91	15:25	28-Jun-91	11:30	20.1	3.9	4.700
0 E	27-Jun-91	10:45	28-Jun-91	12:05	25.3	3.9	5.928
0 UC	27-Jun-91	16:10	28-Jun-91	12:35	20.4	3.9	4.778
0 B	27-Jun-91	17:05	28-Jun-91	13:15	20.2	3.9	4.719
1 S	01-Jul-91	10:20	02-Jul-91	11:15	24.9	3.9	5.831
1 J	01-Jul-91	10:35	02-Jul-91	11:45	25.2	3.9	5.889
1 E	01-Jul-91	11:05	02-Jul-91	12:15	25.2	3.9	5.889
1 UC	01-Jul-91	11:30	02-Jul-91	12:50	25.3	3.9	5.928
1 B	01-Jul-91	12:00	02-Jul-91	13:25	25.4	3.9	5.948
2 S	02-Jul-91	11:20	03-Jul-91	11:35	24.3	3.9	5.675
2 J	02-Jul-91	11:50	03-Jul-91	12:15	24.4	3.9	5.714
2 E	02-Jul-91	12:20	03-Jul-91	12:50	24.5	3.9	5.733
2 UC	02-Jul-91	12:55	03-Jul-91	13:45	24.8	3.9	5.811
2 B	02-Jul-91	13:30	03-Jul-91	14:15	24.8	3.9	5.792
3 S	03-Jul-91	11:37	04-Jul-91	10:35	23.0	3.9	5.374
3 J	03-Jul-91	12:17	04-Jul-91	11:25	23.1	3.9	5.413
3 E	03-Jul-91	12:52	04-Jul-91	13:05	24.2	3.9	5.667
3 UC	03-Jul-91	13:47	04-Jul-91	13:32	23.8	3.9	5.558
3 B	03-Jul-91	14:17	04-Jul-91	12:55	22.6	3.9	5.296
4 S	04-Jul-91	10:50	05-Jul-91	12:15	25.4	3.9	5.948
4 J	04-Jul-91	11:30	05-Jul-91	12:37	25.1	3.9	5.877
4 E	04-Jul-91	12:00	05-Jul-91	13:00	25.0	3.9	5.850
4 UC	04-Jul-91	12:30	05-Jul-91	13:30	25.0	3.9	5.850
4 B	04-Jul-91	13:00	05-Jul-91	14:00	25.0	3.9	5.850

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School;
 E = Exeter Union High School; UC = University of California Lindcove Field
 Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY							
SAMPLE COLLECTION DATA							
Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m ³)
5 S	08-Jul-91	11:00	09-Jul-91	11:15	24.3	3.9	5.675
5 J	08-Jul-91	11:30	09-Jul-91	11:45	24.3	3.9	5.675
5 E	08-Jul-91	12:15	09-Jul-91	12:14	24.0	3.9	5.612
5 UC	08-Jul-91	12:50	09-Jul-91	13:15	24.4	3.9	5.714
5 B	08-Jul-91	13:30	09-Jul-91	13:45	24.3	3.9	5.675
6 S	09-Jul-91	11:17	10-Jul-91	11:20	24.1	3.9	5.628
6 J	09-Jul-91	11:48	10-Jul-91	11:50	24.0	3.9	5.624
6 E	09-Jul-91	12:35	10-Jul-91	12:40	24.1	3.9	5.636
6 UC	09-Jul-91	13:20	10-Jul-91	13:05	23.8	3.9	5.558
6 B	09-Jul-91	14:00	10-Jul-91	13:45	23.8	3.9	5.558
7 S	10-Jul-91	11:20	11-Jul-91	11:30	24.2	3.9	5.655
7 J	10-Jul-91	11:50	11-Jul-91	12:00	24.2	3.9	5.655
7 E	10-Jul-91	12:40	11-Jul-91	12:46	24.1	3.9	5.639
7 UC	10-Jul-91	13:05	11-Jul-91	13:15	24.2	3.9	5.655
7 B	10-Jul-91	13:45	11-Jul-91	13:50	24.1	3.9	5.636
8 S	11-Jul-91	11:30	12-Jul-91	10:50	23.3	3.9	5.460
8 J	11-Jul-91	12:00	12-Jul-91	11:15	23.3	3.9	5.441
8 E	11-Jul-91	12:45	12-Jul-91	11:50	23.1	3.9	5.402
8 UC	11-Jul-91	13:15	12-Jul-91	12:20	23.1	3.9	5.402
8 B	11-Jul-91	13:50	12-Jul-91	13:05	23.3	3.9	5.441
9 S	15-Jul-91	11:15	16-Jul-91	11:45	24.5	3.9	5.733
9 J	15-Jul-91	11:45	16-Jul-91	12:15	24.5	3.9	5.733
9 E	15-Jul-91	12:15	16-Jul-91	12:50	24.6	3.9	5.753
9 UC	15-Jul-91	12:45	16-Jul-91	12:30	23.8	3.9	5.558
9 B	15-Jul-91	13:15	16-Jul-91	14:00	24.8	3.9	5.792

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School;
E = Exeter Union High School; UC = University of California Lindcove Field
Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m³)
10 S	16-Jul-91	11:45	17-Jul-91	11:30	23.8	3.9	5.558
10 J	16-Jul-91	13:05	17-Jul-91	12:00	22.9	3.9	5.363
10 E	16-Jul-91	12:50	17-Jul-91	12:35	23.8	3.9	5.558
10 UC	16-Jul-91	13:30	17-Jul-91	13:10	23.7	3.9	5.538
10 B	16-Jul-91	14:00	17-Jul-91	13:45	23.8	3.9	5.558
11 S	17-Jul-91	11:30	18-Jul-91	11:30	24.0	3.9	5.616
11 J	17-Jul-91	12:00	18-Jul-91	12:00	24.0	3.9	5.616
11 E	17-Jul-91	12:35	18-Jul-91	12:35	24.0	3.9	5.616
11 UC	17-Jul-91	13:10	18-Jul-91	13:10	24.0	3.9	5.616
11 B	17-Jul-91	13:45	18-Jul-91	13:45	24.0	3.9	5.616
12 S	18-Jul-91	11:30	19-Jul-91	11:20	23.8	3.9	5.577
12 J	18-Jul-91	12:00	19-Jul-91	11:50	23.8	3.9	5.577
12 E	18-Jul-91	12:35	19-Jul-91	12:25	23.8	3.9	5.577
12 UC	18-Jul-91	13:10	19-Jul-91	12:50	23.7	3.9	5.538
12 B	18-Jul-91	13:45	19-Jul-91	13:15	23.5	3.9	5.499
13 S	22-Jul-91	11:15	23-Jul-91	11:45	24.5	3.9	5.733
13 J	22-Jul-91	11:45	23-Jul-91	12:20	24.6	3.9	5.753
13 E	22-Jul-91	12:30	23-Jul-91	12:55	24.4	3.9	5.714
13 UC	22-Jul-91	13:00	23-Jul-91	13:30	24.5	3.9	5.733
13 B	22-Jul-91	13:30	23-Jul-91	14:00	24.5	3.9	5.733
14 S	23-Jul-91	11:45	24-Jul-91	11:30	23.8	3.9	5.558
14 J	23-Jul-91	12:20	24-Jul-91	12:00	23.7	3.9	5.538
14 E	23-Jul-91	12:55	24-Jul-91	12:40	23.8	3.9	5.558
14 UC	23-Jul-91	13:30	24-Jul-91	13:10	23.7	3.9	5.538
14 B	23-Jul-91	14:00	24-Jul-91	13:45	23.8	3.9	5.558

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School;
 E = Exeter Union High School; UC = University of California Lindcove Field
 Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY							
SAMPLE COLLECTION DATA							
Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m ³)
15 S	24-Jul-91	11:30	25-Jul-91	11:45	24.3	3.9	5.675
15 J	24-Jul-91	12:00	25-Jul-91	12:15	24.3	3.9	5.675
15 E	24-Jul-91	12:40	25-Jul-91	12:45	24.1	3.9	5.636
15 UC	24-Jul-91	13:10	25-Jul-91	13:25	24.3	3.9	5.675
15 B	24-Jul-91	13:45	25-Jul-91	13:45	24.0	3.9	5.616
16 S	25-Jul-91	11:45	26-Jul-91	11:50	24.1	3.9	5.636
16 J	25-Jul-91	12:15	26-Jul-91	12:46	24.5	3.9	5.737
16 E	25-Jul-91	12:45	26-Jul-91	13:25	24.7	3.9	5.772
16 UC	25-Jul-91	13:25	26-Jul-91	12:10	22.8	3.9	5.324
16 B	25-Jul-91	13:45	26-Jul-91	14:45	25.0	3.9	5.850

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School;
E = Exeter Union High School; UC = University of California Lindcove Field
Station; B = ARB Ambient Air Monitoring Station (background)

APPENDIX B
APPLICATION MONITORING REPORT

State of California

AIR RESOURCES BOARD

METHIDATHION APPLICATION MONITORING REPORT

Ambient Air Monitoring in Tulare County for Methidathion
in July, 1991, after Application to an Orange Grove

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C91-079A

Report Date: December 6, 1991

APPROVED:

J. E. Bell, Project Engineer
Testing Section

Peter K. Oushida, Manager
Testing Section

George Lau, Chief
Engineering Evaluation Branch

This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Methidathion Monitoring in Tulare County in July, 1991

This report presents the results of ambient monitoring for methidathion after a ground application at a selected orchard in Tulare County. The results are based on samples collected by the Air Resources Board (ARB) staff and analyzed by the staff of the Engineering Research Institute (ERI) at the California State University, Fresno (CSUF.) The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

The project engineer was Don Fitzell. The Instrument Technician was Jack Rogers of the ARB. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses was performed by the Engineering Research Institute at CSUF.

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State of California
Air Resources Board

Methidathion Monitoring in Tulare County

I. INTRODUCTION

At the request of the California Department of Pesticide Regulations (DPR), formerly the Department of Food and Agriculture, and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a two-day source impacted ambient monitoring program for methidathion and its breakdown product, methidaoxon, in Tulare County during the month of July 1991.

II. PESTICIDE DESCRIPTION

Methidathion (molecular weight 303.33 g/mole) is an organophosphorus insecticide which is colorless crystal with a melting point of 39-40°C. It is slightly volatile (vapor pressure 3.37×10^{-6} mm Hg at 25°C) and soluble in water only to the extent of 240 ppm at 20°C. It is readily soluble in acetone, benzene and methanol.

Methidathion is a restricted use pesticide under Title 3, California Code of Regulations, Section 6400. The EPA has classified it in Toxicity Category I for oral exposure, Category II for inhalation and Category III for dermal exposure.

Methdathion is used on a variety of crops. It is used on oranges to control red scale and other pests. It is typically applied with tractor-driven equipment at rates from one-quarter to one-half pound per 100 gallons of water.

III. SAMPLING LOCATIONS

An orange grove was selected (FIGURE I.) by Bob Felts of Leffingwell Ag. Sales Co., Inc. and approved by ARB staff to use for application monitoring. The prevailing wind in the area is from the northwest. Three samplers were set up: 1) approximately 25 yards north of the orchard, 2) approximately 15 yards southeast of the orchard and 3) approximately 150 yards southeast of the orchard. A meteorological station was set up near the farthest downwind sampler.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-2 tubes (see APPENDIX II.) These tubes are 8mm x 110mm, with 400 mg in the primary section and with 200

mg in the secondary (SKC catalog #226-30-06). Any methidathion present in the sampled ambient air is captured by the XAD-2 adsorbent contained in the tubes. Subsequent to sampling, the tubes were transported in an iced container to the CSUF's Engineering Research Institute in Fresno for analysis.

Sampling trains designed to operate continuously were set up at the three sampling sites identified in FIGURE II. of this report. Duplicate samples were obtained from all three sites. Sampling tubes were changed according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX A.)

Each sample train consisted of an XAD-2 tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 12VDC vacuum pump. A diagram of the sampling train is shown in FIGURE III. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were wrapped around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that a flow rate of 1.85 lpm was actually achieved when the rotometers were set to 2.0 lpm.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-2 tubes recovered from each sampler were analyzed by the CSUF Engineering Research Institute staff. The XAD-2 in the primary section of each sample tube was extracted with toluene, followed by GC separation on a DB-5 capillary column and measurement by Electron Capture Detector (APPENDIX III.) The secondary (backup) sections were saved to check for breakthrough, if necessary.

VI. RESULTS

Results for methidathion are shown in TABLE I. and a summary of the results along with meteorological data is shown in TABLE III. The results for the breakdown product, methidaoxon, is shown in TABLE II.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the S.O.P. for methidathion (APPENDIX III.)

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX A.) were followed with two exceptions: 1) monitoring was conducted for only 48-hours rather than continuing through Sunday morning, July 14 and 2) no field spike was prepared.

TABLE I. METHIDATHION MONITORING DATA

SAMPLE ID	SAMPLE TIME (HR.)	FLOW RATE (l/min.)	SAMPLE VOLUME (m ³)	MASS DETECTED (ug)	CONCENTRATION (ug/m ³)	Date Approx. Time
0N	1.00	1.85	0.11	ND	--	(background)
0SW1	1.00	1.85	0.11	ND	--	7/10
0SW2	1.00	1.85	0.11	ND	--	1500 - 1600
1N	7.75*	1.85	0.86	0.28	0.33	(application)
1SW1	7.83*	1.85	0.87	ND	--	7/10-11
1SW2	7.92*	1.85	0.88	ND	--	2330 - 0900
2N	2.00	1.85	0.22	0.19	0.86	
2SW1	2.00	1.85	0.22	ND	--	7/11
2SW2	2.00	1.85	0.22	ND	--	0900 - 1100
3N	3.83	1.85	0.42	0.59	1.40	
3SW1	3.83	1.85	0.42	ND	--	7/11
3SW2	3.83	1.85	0.42	ND	--	1100 - 1500
4N	6.83	1.85	0.76	0.62	0.82	
4SW1	6.83	1.85	0.76	0.95	1.25	7/11
4SW2	6.83	1.85	0.76	0.21	0.28	1500 - 2130
5N	10.08	1.85	1.12	3.54	3.16	
5SW1	10.17	1.85	1.13	0.68	0.60	7/11-12
5SW2	10.17	1.85	1.13	0.11	0.10	2130 - 0730
5B	BLANK	--				
6N	23.92	1.85	2.66	1.23	0.46	
6SW1	23.83	1.85	2.64	0.78	0.30	7/12-13
6SW2	23.75	1.85	2.64	ND	--	0730 - 0730

ND = Not Detected; below 0.1 ug/sample.

*Based on the application starting at 0100.








TABLE II. METHIDAOXON MONITORING DATA

SAMPLE ID	SAMPLE TIME (HR.)	FLOW RATE (l/min.)	SAMPLE VOLUME (m ³)	MASS DETECTED (ug)	CONCENTRATION (ug/m ³)	Date Approx. Time
0N	1.00	1.85	0.11	ND	--	(background)
0SW1	1.00	1.85	0.11	ND	--	7/10
0SW2	1.00	1.85	0.11	ND	--	1500 - 1600
1N	7.75*	1.85	0.86	ND	--	(application)
1SW1	7.83*	1.85	0.87	ND	--	7/10-11
1SW2	7.92*	1.85	0.88	ND	--	2330 - 0900
2N	2.00	1.85	0.22	ND	--	
2SW1	2.00	1.85	0.22	ND	--	7/11
2SW2	2.00	1.85	0.22	ND	--	0900 - 1100
3N	3.83	1.85	0.42	ND	--	
3SW1	3.83	1.85	0.42	ND	--	7/11
3SW2	3.83	1.85	0.42	ND	--	1100 - 1500
4N	6.83	1.85	0.76	0.25	0.33	
4SW1	6.83	1.85	0.76	0.27	0.36	7/11
4SW2	6.83	1.85	0.76	ND	--	1500 - 2130
5N	10.08	1.85	1.12	0.29	0.26	
5SW1	10.17	1.85	1.13	ND	--	7/11-12
5SW2	10.17	1.85	1.13	ND	--	
5B	BLANK	--				2130 - 0730
6N	23.92	1.85	2.66	0.62	0.23	
6SW1	23.83	1.85	2.64	0.49	0.19	7/12-13
6SW2	23.75	1.85	2.64	ND	--	0730 - 0730

ND = Not Detected; below 0.25 ug/sample.

*Based on the application starting at 0100.

TABLE III. SUMMARY OF METHIDATHION DATA

Concentration ($\mu\text{g}/\text{m}^3$)			
	Site "N" wind	Site "SW1"	Site "SW2"
(0)	 NW 5 mph	---	---
(1)	0.33  SW 1 mph	---	---
(2)	0.86  SW 4 mph	---	---
(3)	1.40  W/SW 4 mph	---	---
(4)	0.82  NW 3 mph	1.25	0.28
(5)	3.16  SW 1 mph	0.60	0.10
(6)	0.46  SW/NW/E/S 3 mph	0.30	---

--- indicates not detected.

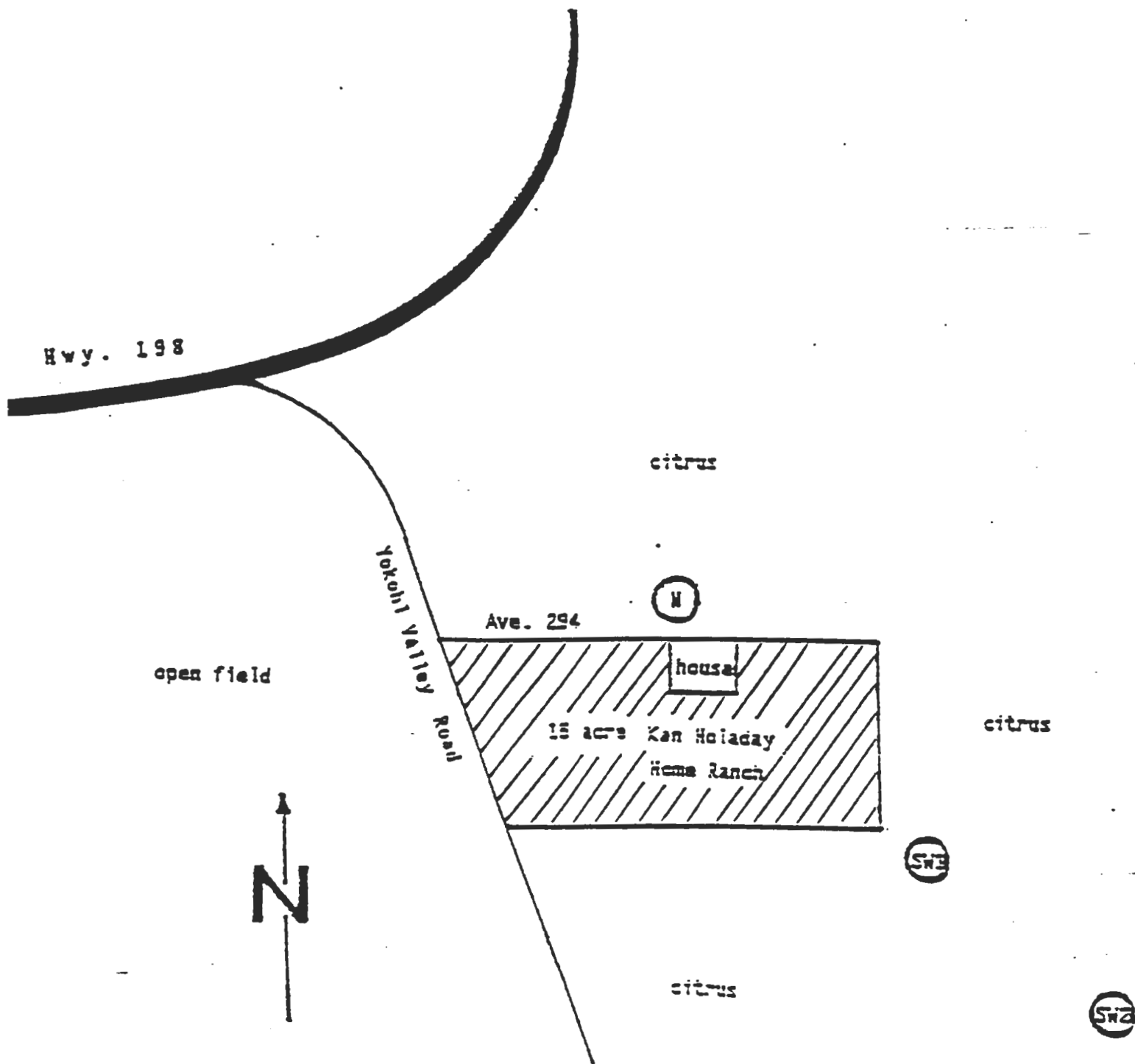
() indicates sampling period.

Arrowhead indicates direction wind is blowing toward.

A map showing the application site area. The map includes the following features:

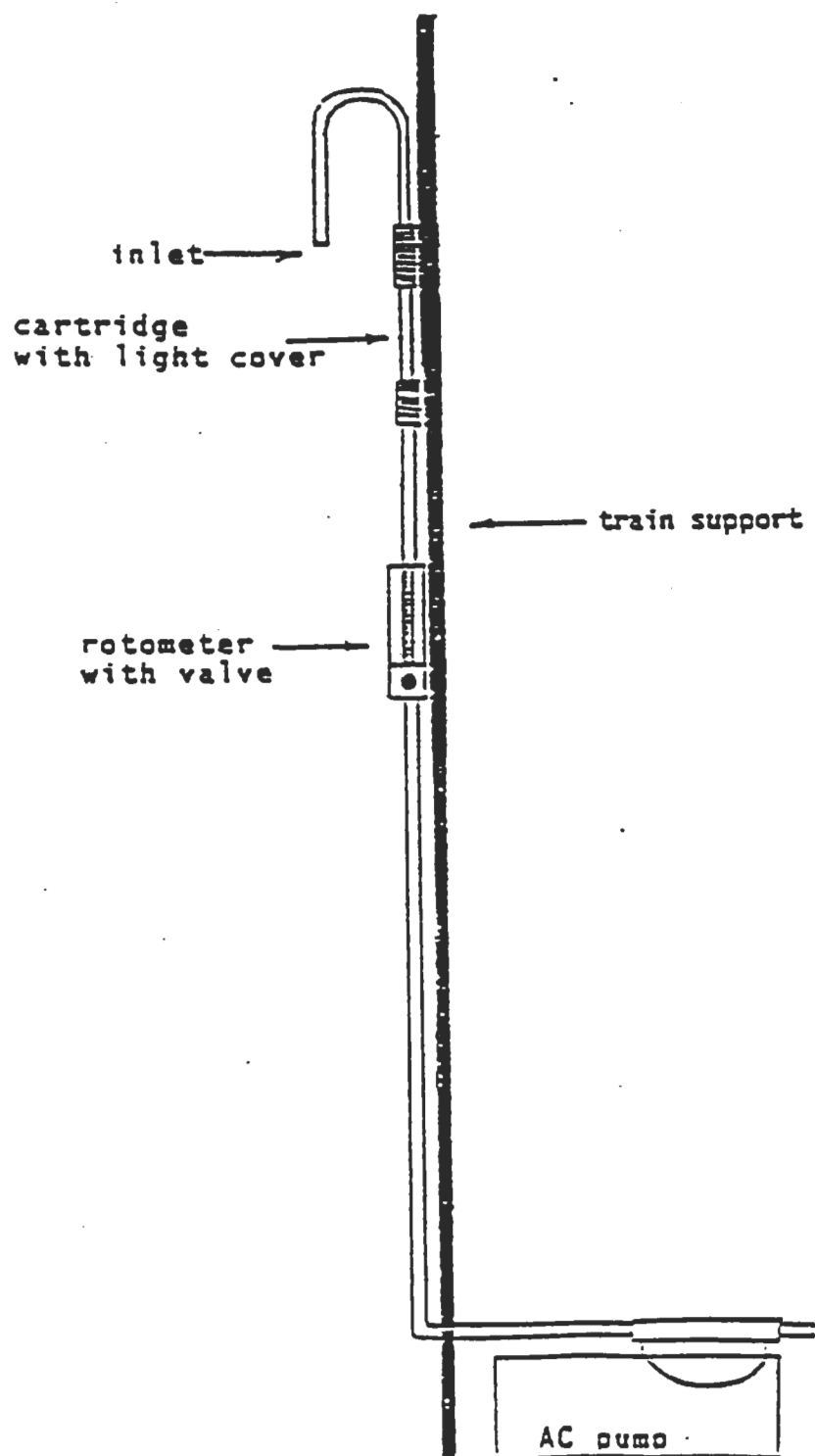
- Communities:** WOODLAKE (top center), LINDSAY (bottom center), and STRATHMORE (bottom right).
- Roads:**
 - Highway 216 (top left)
 - Highway 198 (middle left)
 - Rd. 212 (vertical, top center)
 - Rd. 100 (vertical, bottom left)
 - Highway 66 (vertical, bottom left)
 - Rd. 204 (vertical, bottom center)
 - Ave. 232 (horizontal, bottom center)
 - Ave. 196 (horizontal, bottom right)
 - Ave. 178 (horizontal, bottom right)
 - Yokel Valley Rd. (diagonal, middle right)
- Water Bodies:** Lake Kaweah (top right).
- Application Site:** Indicated by a black triangle on Yokel Valley Rd., between Highway 198 and Ave. 232.
- Other Labels:** "FOSTER" (bottom left, possibly a road or area name).

FIGURE II. PESTICIDE MONITORING SITES



- N = "upwind" sampler
SW1 = closest "downwind" sampler
SW2 = farthest "downwind" sampler

FIGURE III. PESTICIDE SAMPLING APPARATUS



APPENDIX I.

MONITORING OF PESTICIDES IN AIR -- 1991 METHIDATHION AND METHIDAOXON APPLICATION MONITORING

SAMPLE RESULTS -- SUMMARY

Field Log #	Field ID	Lab Number	Methidaoxon ug	Methidathion ug
1	0 N	91-46A. 1	ND	ND
2	0 SW1	91-46A. 3	ND	ND
3	0 SW2	91-46A. 5	ND	ND
4	1 N	91-46A. 7	ND	0.28
5	1 SW1 *	91-46A. 9	ND	ND
5	1 SW1 *	91-46A. 10	ND	ND
6	1 SW2	91-46A. 11	ND	ND
7	2 N	91-46A. 13	ND	0.19
8	2 SW1	91-46A. 15	ND	ND
9	2 SW2	91-46A. 17	ND	ND
10	3 N	91-46A. 19	ND	0.59
11	3 SW1	91-46A. 21	ND	ND
12	3 SW2	91-46A. 23	ND	ND
13	4 N	91-46A. 25	0.25	0.62
14	4 SW1	91-46A. 27	0.27	0.95
15	4 SW2 *	91-46A. 29	ND	0.21
15	4 SW2 *	91-46A. 30	ND	0.21
16	5 N	91-46A. 31	0.29	3.54
17	5 SW1 **	91-46A. 33	ND	0.70
17	5 SW1 **	91-46A. 33	ND	0.66
18	5 SW2	91-46A. 35	ND	0.11
19	5 B	91-46A. 37	ND	ND
20	6 N	91-50A. 1	0.62	1.23
21	6 SW1	91-50A. 3	0.49	0.78
22	6 SW2	91-50A. 5	ND	ND
MDL			0.25	0.10

* Duplicate extraction

** Duplicate injection

METHIDATHION AMBIENT AIR MONITORING PROTOCOL

Ambient Air Monitoring for Methidathion in Tulare County

Engineering Research Institute
California State University, Fresno

Date: June 13, 1991

APPROVED:

Brenda R. Rayne
for Engineering Research Institute, CSUF

Peter V. Vachon
for Air Resources Board

Ralph Propper

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Methidathion (Supracide) Protocol

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the California State University, Fresno (CSUF) and the Air Resources Board (ARB) staff will conduct an ambient air monitoring program for Methidathion and its breakdown product, Methidaoxone in Tulare County. CSUF staff will conduct the four week ambient air monitoring program, perform all laboratory QA/QC activities, analyze all samples collected during the monitoring program, and prepare the report describing the monitoring/analytical procedures and presenting the results. The ARB staff will act in an advisory role to CSUF staff and conduct source impacted air monitoring of a field during application of the pesticide. Analysis of these samples will be done by CSUF. Monitoring results will be used by DFA to decide if Methidathion should be identified as a toxic air contaminant under Section 14022 et seq. of the Food and Agricultural Code.

The peak use of Methidathion will occur during July in Tulare County. Methidathion is used as an insecticide on citrus trees. Monitoring is planned to begin the first week of July, 1991 and continue for four weeks in Tulare County. Samples will only be taken Monday through Friday.

II. Sampling

Field sampling and related QA/QC activities will be conducted by the CSUF staff. Methidathion will be collected on XAD-2 cartridges using the sample train in FIGURE I. Twenty-four hour samples will be collected with a flow rate of approximately 4 liters per minute.

Rotometers will be used to monitor sample flow rates. These rotometers will be calibrated in the laboratory at CSUF prior to the start of monitoring using a digital flowmeter. Each sampler will be leak checked with the sampling media installed prior to and after each twenty-four hour sampling period. Flow rates will be allowed to stabilize before sampling begins and these rates will be recorded in a log book along with beginning and ending times. Any change in the flow rate at the end of the sampling period will also be noted.

Sampling will be conducted at the same sites used for the Naled monitoring in Tulare County (FIGURE II. and TABLE I.) except for Kaweah High School which will not have teaching or maintenance staff during summer recess. An alternate sampling site at Lemon Cove, as well as other potential sites, will be confirmed during the week of sample equipment set up. Selection of the monitoring sites is based upon the siting criteria contained in the ARB Quality Assurance Plan for Pesticide Monitoring (APPENDIX A). Background samples will be collected at the ARB's ambient monitoring site in downtown Visalia. All samples will be stored in an ice chest until delivered to the CSUF laboratory in Fresno for analysis.

During the four week ambient monitoring program, CSUF and ARB staff will also conduct an application monitoring study: ARB staff will conduct field sampling during a pesticide application and CSUF staff will analyze the samples collect during the application. As outlined in the Quality Assurance Plan for Pesticide Monitoring (APPENDIX A.), three samplers will be set up; 1) 15 yards upwind, 2) 15 yards downwind and 3) 150 yards downwind of the applied field. The sample tubes will be changed as specified in the plan. The site of the application will be determined at a later date.

III. Analysis

Analysis of samples will be by the Engineering Research Institute, California State University, Fresno. The samples will be extracted with toluene, then injected into a gas chromatograph with an electron capture detector (ECD). A detailed description of the analytical procedure will be presented in the "Standard Operating Procedure for the Determination of Methidathion and Methidaoxone in Ambient Air."

Quality control information will include: 1) recovery data from at least three samples spiked at three different concentrations, 2) instrument variability based on three replicate injections of a single sample at each of the three spiked concentrations, 3) stability study done with sets of triplicate spiked samples being stored under actual conditions and analyzed at appropriate intervals and 4) conversion/collection efficiency study conducted under field conditions (drawing ambient air through spiked samples at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank.

IV. Quality Assurance

Quality assurance procedures for sampling and analysis will be followed as outlined in ARB's Quality Assurance Plan for Pesticide Monitoring (APPENDIX A.) An additional sampler will be rotated among the sites to provide data on duplicate samples for assessing precision. A chain of custody sheet will accompany all samples. Collection efficiency, stability, reproducibility and limit of detection studies will all be completed by the analytical laboratory prior to sampling. Field blanks and trip spikes will also be supplied to the laboratory by ARB's Quality Assurance Section.

V. ARB Personnel

Technical assistance during set up and sampling will be provided by Don Fitzell of the Engineering Evaluation Branch. Gabe Ruiz of the QA Section will audit the flow rates in the field and provide spiked samples to the laboratory.

VI. CSUF Personnel

The CSUF staff is: Brenda Royce, Clari Cone, Beverly Boucher, Barthelemy Konan and Akhtar Ali.

FIGURE 1. PESTICIDE SAMPLING APPARATUS

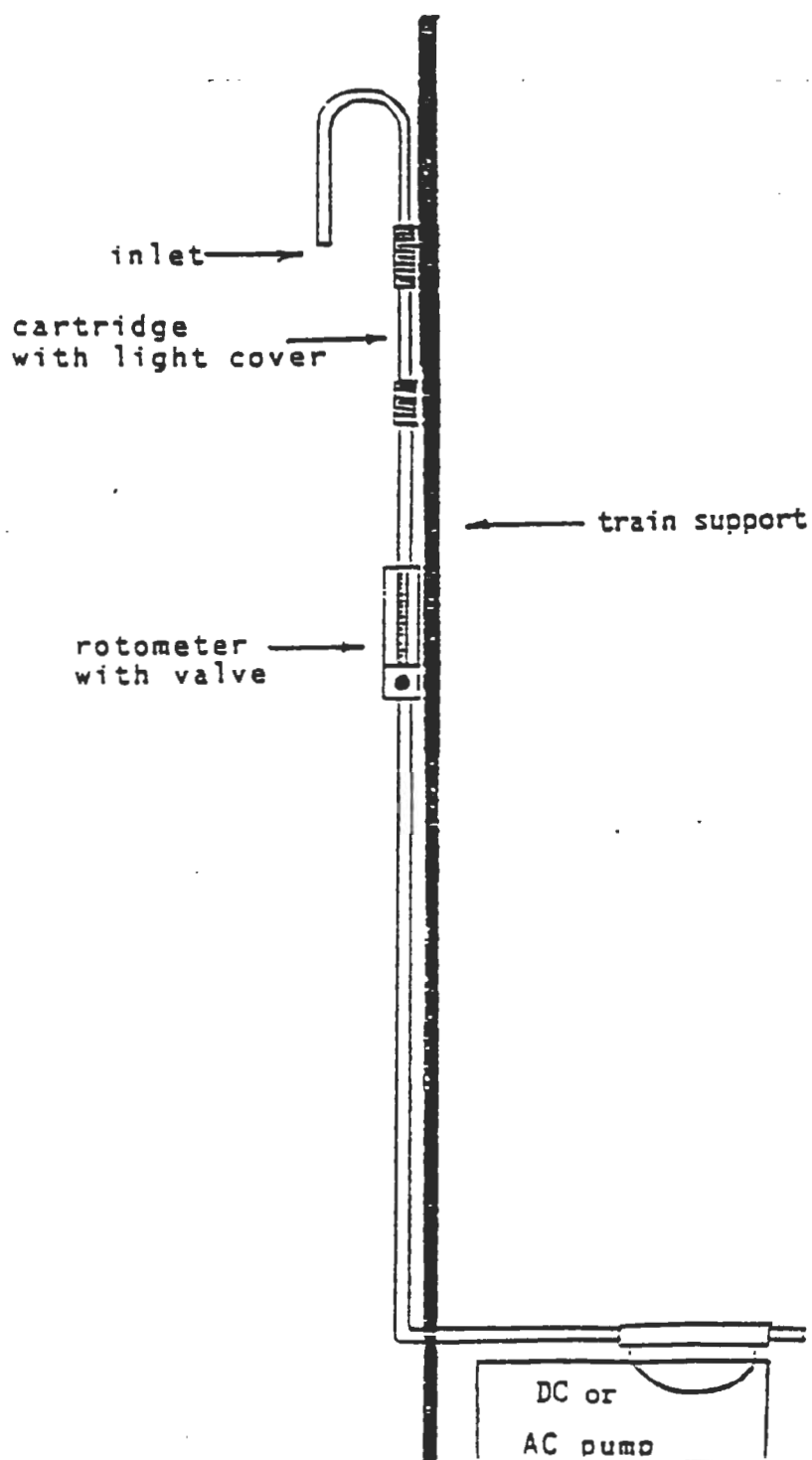


FIGURE II. PROPOSED SAMPLING SITES

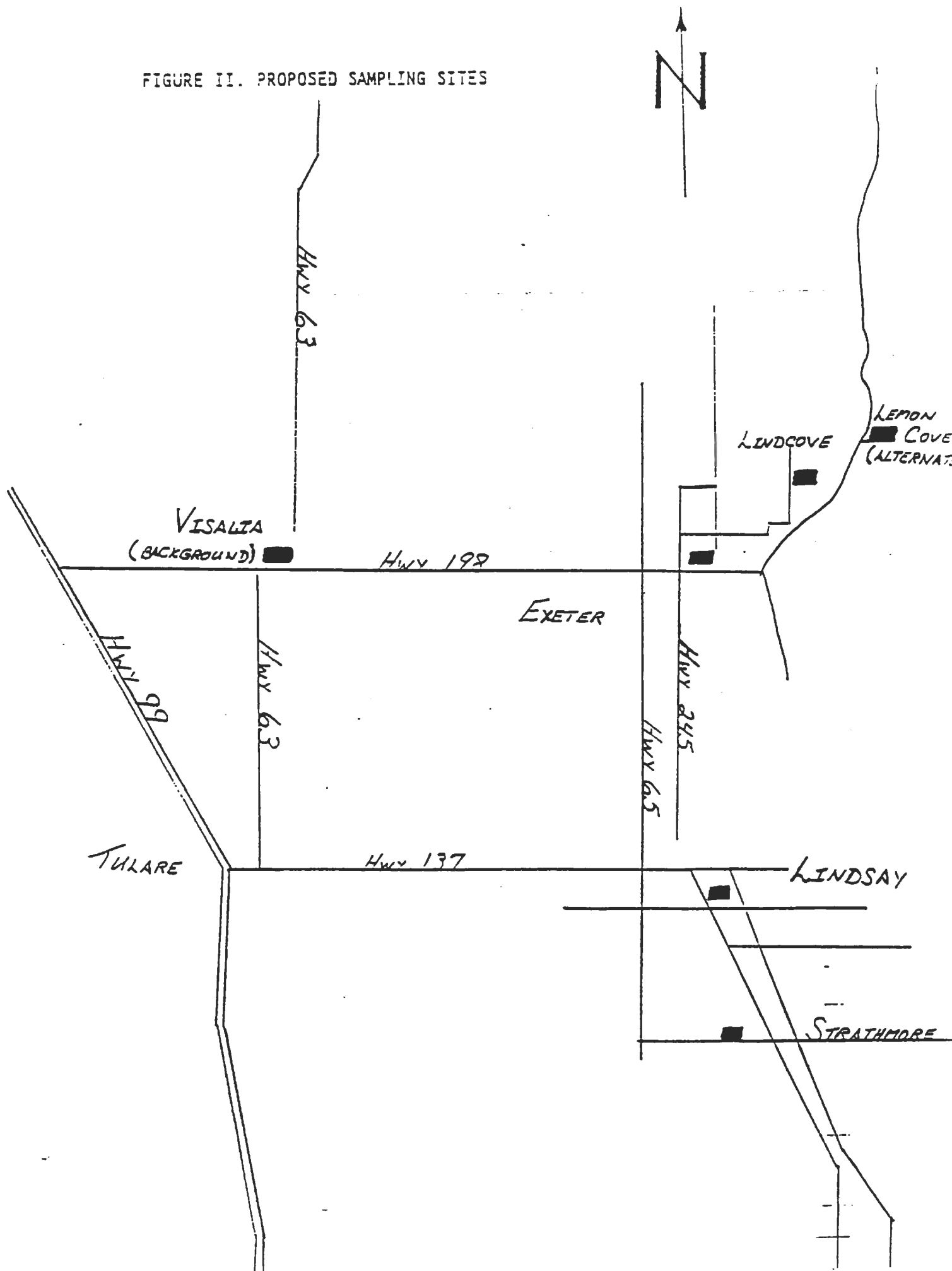


TABLE I. Ambient Sampling Sites Used For Naled

Sunnyside Union Elementary School
21644 Avenue 196
Strathmore, CA 93267

Jefferson Elementary School
333 Westwood Avenue
Lindsay, CA 93247-1801

Kaweah High School
21215 Avenue 300
Exeter, CA 93221

University of California
Lindcove Field Station
22963 Carson Avenue
Exeter, CA 93221

Air Resources Board
Ambient Air Monitoring Station
310 N. Church St.
Visalia, CA
(Background site)

State of California
Air Resources Board

Quality Assurance Plan
for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division
and
Stationary Source Division

September 28, 1990

APPROVED:

Gerriane A. Shuman, Chief,

Toxic Air Contaminant
Identification Branch
Stationary Source Division

[Signature], Chief,
Quality Management and
Operations Support Branch
Monitoring and Laboratory Division

George Lee, Chief,
Engineering Evaluation Branch
Monitoring and Laboratory Division

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. Short-term (one month) ambient monitoring will be conducted in the area of, and during the season of, peak pesticide applications. In addition, monitoring of a field during and after application (up to 72 hours) will occur. The purpose of this document is to specify quality assurance activities for sampling and laboratory analysis of the pesticide.

II. Quality Assurance Policy Statement

It is the policy of the ARB to provide DFA with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

III. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: 1) to establish the necessary quality control activities relating to site selection, sample collection, sample analysis, and data validation, and 2) assessment of data quality in terms of precision, accuracy and completeness.

IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. Background sites should be located away from any applications.

Siting criteria for placement of samplers near a pesticide application for collection of short-term samples are: 1) fifteen yards upwind of the field, 2) fifteen yards downwind of the field, and 3) 150 yards downwind of the field. These are only guidelines, since conditions at the site will dictate the placement of monitoring stations. Data on wind speed and direction will be collected during application monitoring. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed. Field application monitoring will follow the schedule outlined in TABLE 2. This schedule and study design are consistent with requests from DFA for monitoring near a pesticide application.

A. Monitoring Site Description

The protocol for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions).

Similarly, a map or sketch of the monitoring stations should be made with respect to the application field.

V. Sampling

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

A. Protocol

Prior to conducting any pesticide monitoring a protocol will be written that describes the overall monitoring program and includes the following topics:

1. Identification of the sample site locations.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.)
3. Description of the analytical method.
4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.
5. Test schedule.
6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to this specific pesticide.

B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

D. Calibration

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within ± 5 minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours ± 15 minutes.

Flow meters, flow controllers or critical orifices should be calibrated against a referenced flow meter prior to a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within $\pm 10\%$ if a calibrated pressure transducer is used to check the flows, or within $\pm 15\%$ if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of those control limits.

E. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc. should be made by sampling personnel.

TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		<u>Other Spacing Criteria</u>
	<u>Vertical</u>	<u>Horizontal</u>	
2-15	1	1	<ol style="list-style-type: none"> 1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have ungestriated air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

	<u>Samples per Site*</u>		
	<u>-15 yds</u> <u>up-</u> <u>wind</u>	<u>-15 yds</u> <u>down-</u> <u>wind</u>	<u>-150 yds</u> <u>down-</u> <u>wind</u>
- Background sample (1 hr. sample: prior to application).	2	2	2
- Application + 1 hr. after application combined sample.	2	2	2
- 2 hr. sample from 1 to 3 hours after the application.	2	2	2
- 4 hr. sample from 3 to 7 hours after the application.	2	2	2
- 8 + hr. sample from 7 to 15+ hours after the application.	2	2	2
- 9 + hr. sample from 15 to 24+ hours after the application.	2	2	2
- 1st 24 hour sample starting at the end of the 9+ hr. sample.	2	2	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9+ hr. sample.	2	2	-

* duplicate collocated samples at each site.

VI. Analysis

Analytical audits should be conducted by spiking the sample medium with the reference standard. These can then be carried into the field and handled as actual samples (trip spike) or run at the background site for ambient monitoring (field spike) prior to delivery to the laboratory for analysis. At least one spike per monitoring period is required and one spike per week is recommended for ambient monitoring.

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. should include: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures.

A. Standard Operating Procedures

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The monitoring plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable gas standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as; use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of lab analysis and after every tenth sample. Control samples should be found to be within control

limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume from the field data sheet to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in ug/m³ as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum detection limit), total number of samples and number of samples above the minimum detection limit. For this purpose, collocated samples are averaged and treated as a single sample.

A. Quality Assurance

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary. The quality assurance report will include a summary of the average data precision, accuracy, and completeness.

1. Precision and Accuracy

The average precision or standard deviation will be reported based on the comparison of the collocated sampling data. Accuracy data to be reported includes the results of the analyses of spiked samples and the results of any flow audits.

2. Data Completeness

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample time cannot be verified, or if any of the sampling medium is lost during sampling, shipment or analysis.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: _____
Sample/Run #: _____ Time: _____
Plant name: _____
Sample Location: _____
Type of Sample: _____
Log #: _____ Initials: _____

ACTION	DATE	TIME	GIVEN BY	TAKEN BY
Sample Collected				
Transfer				
Transfer				
Transfer				
Transfer for Analysis				

Disposition
of Sample:

Immediate Analysis _____
Storage _____

Refrigerator _____
Freezer _____

RELATED ID'S	DESCRIPTION

RETURN THIS FORM TO: Don Fitzell (445-0618)

APPENDIX III.

ERI Methidathion Analytical S.O.P.

The information in this appendix can be found in the main body of the ERI report.

APPENDIX C
ANALYTICAL RESULTS

Methidathion in Air -- Tulare County ($\mu\text{g}/\text{m}^3$)

Date	Sunnyside Union Elementary				Jefferson Elementary			
	Methidaoxon		Methidathion		Methidaoxon		Methidathion	
	1	2	1	2	1	2	1	2
27-Jun-91	0.042		0.027		0.035		0.032	
01-Jul-91	0.061	0.058	0.023	0.024	0.051		0.018	
02-Jul-91	0.073	0.067	ND	ND	0.11		0.018	
03-Jul-91	0.051	ND	ND	ND	ND		0.012	
04-Jul-91	0.036	ND	ND	ND	0.033		0.011	
08-Jul-91	0.067		ND		0.048	0.077	ND	ND
09-Jul-91	0.084		ND		0.043	0.077	ND	ND
10-Jul-91	0.057		ND		0.11	0.097	0.56	0.56
11-Jul-91	0.033		ND		0.060	0.089	0.29	0.32
15-Jul-91	ND		0.017		ND		0.036	
16-Jul-91	ND		0.020		ND		0.023	
17-Jul-91	ND		ND		0.043		0.036	
18-Jul-91	ND		0.011		ND		0.031	
22-Jul-91	ND		ND		ND		0.028	
23-Jul-91	ND		ND		ND		0.025	
24-Jul-91	ND		0.029		ND		0.015	
25-Jul-91	0.092		ND		0.11		0.014	

LOD: Methidathion -- $0.01 \mu\text{g}/\text{m}^3$
Methidaoxon -- $0.03 \mu\text{g}/\text{m}^3$

LOQ: Methidathion -- $0.03 \mu\text{g}/\text{m}^3$
Methidaoxon -- $0.09 \mu\text{g}/\text{m}^3$

KEY: 1 = Primary sampling tube
2 = Replicate sampling tube

Methidathion in Air -- Tulare County ($\mu\text{g}/\text{m}^3$)

Date	Exeter Union High School				UC Lindcove Field Station			
	Methidaoxon		Methidathion		Methidaoxon		Methidathion	
	1	2	1	2	1	2	1	2
27-Jun-91	0.043		0.019		0.075		0.014	
01-Jul-91	0.037		ND		0.055		ND	
02-Jul-91	0.12		0.028		0.062		ND	
03-Jul-91*	ND		0.012		ND		ND	
04-Jul-91*	—		—		—		—	
08-Jul-91	0.046		ND		0.049		ND	
09-Jul-91	0.039		ND		0.078		ND	
10-Jul-91	ND		ND		ND		ND	
11-Jul-91	0.057		ND		NR**		NR**	
15-Jul-91	ND	ND	0.015	0.011	ND		ND	
16-Jul-91	ND	ND	ND	ND	ND		0.010	
17-Jul-91	ND	ND	ND	ND	ND		ND	
18-Jul-91	ND	ND	0.098	0.042	ND		0.014	
22-Jul-91	ND		0.017		ND	ND	ND	ND
23-Jul-91	ND		ND		ND	ND	ND	ND
24-Jul-91	0.066		ND		ND	ND	ND	ND
25-Jul-91	0.12		ND		ND	ND	ND	0.011

LOD: Methidathion -- $0.01 \mu\text{g}/\text{m}^3$
Methidaoxon -- $0.03 \mu\text{g}/\text{m}^3$

LOQ: Methidathion -- $0.03 \mu\text{g}/\text{m}^3$
Methidaoxon -- $0.09 \mu\text{g}/\text{m}^3$

KEY: 1 = Primary sampling tube
2 = Replicate sampling tube

* These two sites were not accesible on July 4. As a result, the July 3 sample represents a two day sampling period from July 3 to July 5.

** Sample not run; sample tubes broken.

Methidathion in Air -- Tulare County ($\mu\text{g}/\text{m}^3$)

	ARB Monitoring Station (Background)			
	Methidaoxon		Methidathion	
	Date	1	2	1
27-Jun-91	0.041		ND	
01-Jul-91	0.039		0.013	
02-Jul-91	0.066		0.012	
03-Jul-91	ND		ND	
04-Jul-91	0.060		ND	
08-Jul-91	ND		ND	
09-Jul-91	0.056		ND	
10-Jul-91	0.068		ND	
11-Jul-91	ND		ND	
15-Jul-91	ND		ND	
16-Jul-91	ND		ND	
17-Jul-91	ND		ND	
18-Jul-91	ND		ND	
22-Jul-91	ND		ND	
23-Jul-91	ND		ND	
24-Jul-91	0.086		ND	
25-Jul-91	0.11		ND	

LOD: Methidathion – $0.01 \mu\text{g}/\text{m}^3$
Methidaoxon – $0.03 \mu\text{g}/\text{m}^3$

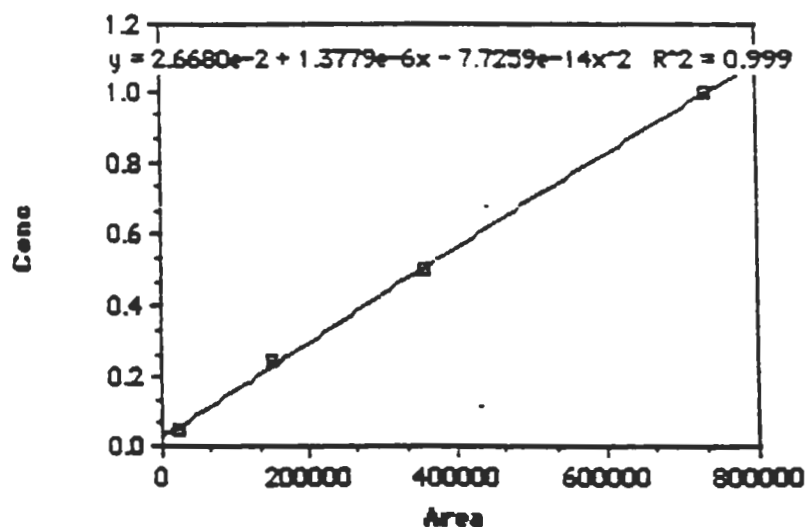
LOQ: Methidathion – $0.03 \mu\text{g}/\text{m}^3$
Methidaoxon – $0.09 \mu\text{g}/\text{m}^3$

KEY: 1 = Primary sampling tube
2 = Replicate sampling tube

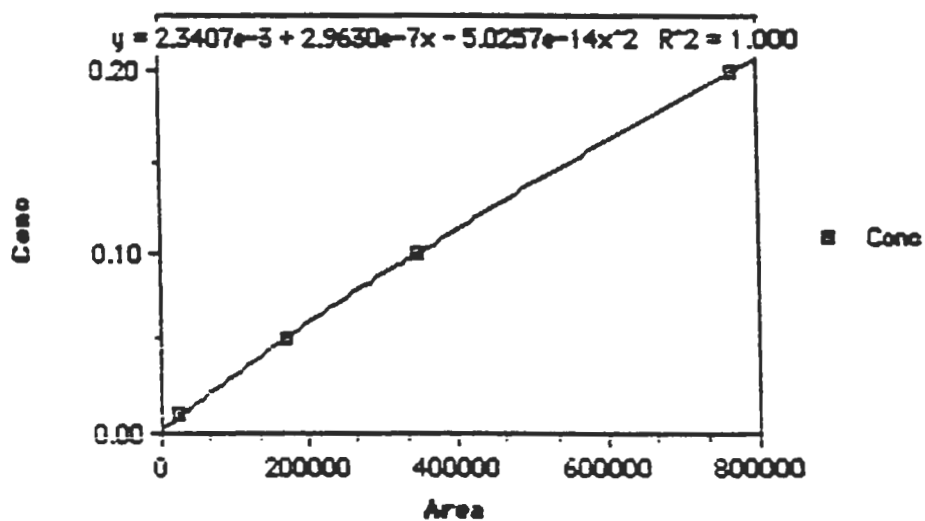
APPENDIX D

STANDARD CURVE EXAMPLE

July 10, 1991 ECD
Methidathion Std Curve



July 10, 1991 ECD
Methidathion Std Curve



Untitled Data #1

Thu, Jul 11, 1991 12:39 PM

Conc	Area	Conc	Area
1.000	735392.000	0.200	767236.000
0.500	358440.000	0.100	347711.000
0.250	150144.000	0.050	169449.000
0.050	25705.000	0.010	24294.000

Standard Curve Equations for Methidathion and Methidathion

WS 155 .01/.05 ME/MEOX

CHANNEL A INJECT 07/10/91 10:10:02

II 1

II 0

7.72

8.30

Methidaoxon

9.34

9.78

Methidathion

ER 0

METHIDATHION/METHIDAOXON

07/10/91 10:10:02

CH= "A" PS= 1.

FILE 1.

METHOD 0.

RUN 100

INDEX 100

PEAK#	AREA%	RT	AREA BC
1	8.801	7.72	4882 01
2	42.734	8.3	23705 01
3	4.669	9.34	2590 01
4	43.796	9.78	24294 01
TOTAL	100.		55471

Working Standard Chromatogram

0.05 ug/mL Methidaoxon; 0.01 ug/mL Methidathion

WS 155 .05/.250 ME/MEOX

CHANNEL A INJECT 07/10/91 09:55:50

II 1

II 0

8.30 Methidaoxon

9.74

9.78 Methidathion

ER 0

METHIDATHION/METHIDAOXON 07/10/91 09:55:50 CH= "A" PS= 1

FILE 1. METHOD 0. RUN 99 INDEX 99

PEAK#	AREA%	RT	AREA BC
1	46.658	8.3	150144 01
2	0.685	9.34	2205 01
3	52.657	9.78	169449 01

TOTAL 100. 321798

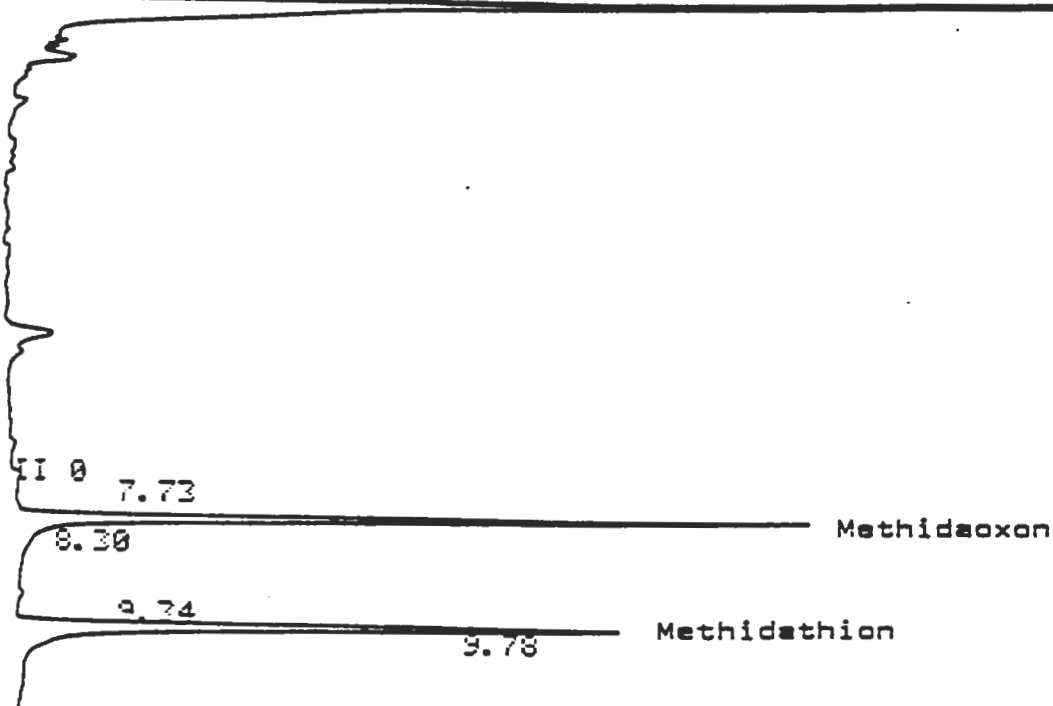
Working Standard Chromatogram

0.25 ug/mL Methidaoxon; 0.05 ug/mL Methidathion

WS 154 .10/.50 ME/MEOX

CHANNEL A INJECT 07/10/91 09:41:36

II 1



ER 0

METHIDATHION/METHIDAOXON 07/10/91 09:41:36 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 98 INDEX 98

PEAK#	AREA%	RT	AREA BC
1	1.165	7.73	8352 01
2	49.981	8.3	358440 01
3	0.37	9.34	2652 01
4	48.485	9.78	347711 01
TOTAL	100.		717155

Working Standard Chromatogram

0.5 ug/mL Methidaoxon; 0.1 ug/mL Methidathion

WS 153 .20/1.0 ME/MEOX

CHANNEL A INJECT 07/10/91 09:27:10

II 1

II 0

7.74

Methidaoxon

8.29

9.33

Methidathion

9.77

ER 0

METHIDATHION/METHIDAOXON 07/10/91 09:27:10 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 97 INDEX 97

PEAK#	AREA%	RT	AREA	BC
1	1.117	7.74	16999	02
2	48.324	8.29	735392	03
3	0.143	9.33	2174	01
4	50.416	9.77	767236	01
TOTAL	100.		1521801	

Working Standard Chromatogram

1.0 ug/mL Methidaoxon; 0.2 ug/mL Methidathion

APPENDIX E

QUALITY ASSURANCE REPORT

March 31, 1993

Audit Report
Methidathion and Methidaoxon Monitoring in Tulare County

SUMMARY

Field Audit

On June 27, 1991, staff of the Quality Assurance Section of the California Air Resources Board conducted a field audit of the five samplers used in the ambient air monitoring of Methidathion and Methidaoxon by the Engineering Research Institute of the California State University, Fresno. The audit consisted of an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring, and an evaluation of the flow rate accuracy of each sampler with a mass flow meter traceable to the National Institute of Standards and Technology.

The siting criteria were met in most cases with the following exceptions: all the samplers were located within 20 meters of a tree dripline, but in every case the distance between the sampler and the tree was more than twice the height that the tree protruded above the sampler; the probe of the sampler at the University of California field station in Lindcove was only 1.8 meters above the ground; and the sampler at the Exeter High School was located within 3.5 meters of a pair of smokestacks which protruded about 2 meters above the sampler's inlets, and whose operational status was unknown.

The flow rate audits resulted in an average percent difference of 1.4%, with individual differences ranging from -0.9% to 4.2%. The records for field operations were appropriate and consistent with good practice.

In addition, the samplers used by the Air Resources Board's Engineering Evaluation Branch staff in the monitoring of a Methidathion application were audited before and after the sampling period. The difference between the reported and the true flow rates averaged 1.7% with a range of 0% to 3.4% in the pre-application audit, and 1.7% with a range of 0.5% to 2.7% after the application.

Laboratory Audit

An audit of the laboratory operations in support of the Methidathion and Methidaoxon monitoring project was conducted between July 10, 1991 and June 8, 1992. The laboratory audit was composed of both a system and an analytical performance audit. The system audit consisted of a review of the laboratory instrumentation used for the project and the quality control measures pertaining to sample handling, analysis and documentation. For the analytical performance audit, XAD-2 resin tubes were spiked with Methidathion and Methidaoxon by QA staff and submitted to the laboratory for analysis.

In general, good quality control practices were followed in the study. The sampling, sample handling and storage, method validation, and documentation were adequate.

The results of the analytical audit for Methidathion showed a positive bias averaging 16.7% and ranging from 11.5% to 23.1%. The results for the Methidaoxon audit showed an average difference of 16.5% with a range of -1.2% to 42.9%. It is speculated that the positive biases were caused by interferences in the method, and further studies may be necessary to characterize the magnitude and possible source of the interference.

Audit Report
Methidathion and Methidaoxon Monitoring in Tulare County

FIELD AUDIT

On June 27, 1991, Gabriel Ruiz of the Quality Assurance (QA) Section of the California Air Resources Board (ARB) conducted a field audit of the five samplers used in the Methidathion and Methidaoxon air monitoring project by the Engineering Research Institute (ERI) of the California State University, Fresno. The audit consisted of an evaluation of the flow rate accuracy of each sampler, and an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring prepared by the Monitoring and Laboratory Division (MLD) and the Stationary Source Division (SSD).

Sampler Siting

The five monitoring sites were located at the ARB air monitoring station in Visalia, the Exeter High School in Exeter, the University of California field station in Lindcove, the Jefferson Elementary School in Lindsay, and the Sunnyside Union Elementary School in Strathmore. The sites were selected by the MLD's Engineering Evaluation Branch (EEB) staff, following the guidelines specified in the Quality Assurance Plan for Pesticide Monitoring.

Three deviations from the siting criteria were observed (see Table 1). First, all the samplers were located within 20 meters of a tree dripline; however, in all cases the distance between the tree and the sampler was more than twice the height that the tree protruded above the sampler's probe. Second, the sampler's probe at the University of California field station in Lindcove was only 1.8 meters above the ground. While it is not likely that the probe's height had an effect on the integrity of the samples, an effort should be made to conform with the established siting criteria, so that uniformity can be maintained. And third, the sampler at the Exeter High School was located within 3.5 meters of a pair of smokestacks which protruded about 2 meters above the sampler's inlets. The operational status of the stacks was unknown at the time of the audit.

Table 1. Summary of the samplers' conformance with the siting criteria during the ambient monitoring of Methidathion.

Site Location	Height from ground 2-15 meters	Distance from supporting structure Vertical/Horizontal 1 meter	20 meters from tree dripline	Distance from obstacles larger than two times the height the obstacle protrudes above the sampler	Unrestricted airflow 270 degrees around the sampler	10 meters from incineration flue
Vicella-ARB Monitoring Station 310 N. Church Street Vigil, CA Exter High School Exeter, CA	Yes	Yes	1 No	Yes	Yes	Yes
U.C. Field Station - Lindcove 2203 Carreon Avenue Exeter, CA	Yes	Yes	2 No	Yes	Yes	3 No
Jefferson Elementary School 333 Westwood Avenue Lindsey, CA	4 No	Yes	5 No	Yes	Yes	Yes
Sunnyside Union Elementary School 21644 Avenue 196 Strathmore, CA	Yes	Yes	6 No	Yes	Yes	Yes
	Yes	Yes	7 No	Yes	Yes	Yes

- NOTES:
1. Sampler was 7.5 m from tree dripline. The tree protruded about 3 m above the sampler's probe.
 2. Sampler was 16.8 m from tree dripline. The tree protruded about 0.6 m above the sampler's probe.
 3. Sampler was 3.4 m from smokestacks.
 4. Sampler probe was about 1.8 m from ground.
 5. Sampler was 16.5 m from tree dripline. The tree protruded about 0.5 m above the sampler's probe.
 6. Sampler was 15.5 m from tree dripline. The tree protruded about 6 m above the sampler's probe.
 7. Sampler was 16.8 m from tree dripline. The tree protruded about 3 m above the sampler's probe.

Field Operations

Sample collection and other field operations were carried out by Barthelemy Konan of the ERI. The sampling apparatus consisted of two XAD-2 resin tubes, each connected with latex tubing to a rotameter. The rotameters were then connected with latex tubing to a single pump. The assembly was supported with a 2 meter section of aluminum tubing (see Figure 1). The adsorbant tubes were covered with aluminum foil to protect them from sunlight.

Before deploying the samplers in the field, a single-point calibration of the rotameters was performed by setting the flow rate at 4.0 liters per minute (lpm) and measuring the actual flow with a bubble meter. The measured flow rate was then reported as the sample collection flow rate.

The audit was conducted on the same day that the samplers were set up and background sampling was initiated, thus the sampling records available at the time were limited to sampler location, date start time, and initial flow rate. Information to be collected later included stop time, final flow rate, and comments about unusual conditions. The records for field operations were appropriate and consistent with good practice.

Flow Rate Audits

A flow rate audit of the samplers used by the ERI was conducted in the field with a 0-10 lpm mass flow meter certified against a primary standard gas flow calibration system traceable to the National Institute of Standards and Technology (NIST). The audit was conducted following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 1.4% and ranged from -0.9% to 4.2% (Table 2).

Also, three samplers used by the EEB in the monitoring of a Methidathion application were audited at the EEB's shop prior to the application on July 3, 1991, and after the application on July 15, 1991.

A single-point calibration of the rotameters was performed by the EEB staff by setting the flow rate at 2.0 lpm and measuring the actual flow with a bubble meter. The average of the measured flows was then assigned as the sample collection flow rate. The flow rates were audited with a NIST traceable 0-3 lpm mass flow meter (see Attachment I). The difference between the reported and the true flow rates in the pre-application audit averaged 1.7% and ranged from 0% to 3.4% (Table 3). The post-application audit results confirmed the rotameters' stability with an average difference of 1.7% and a range of 0.5% to 2.7% (Table 4).

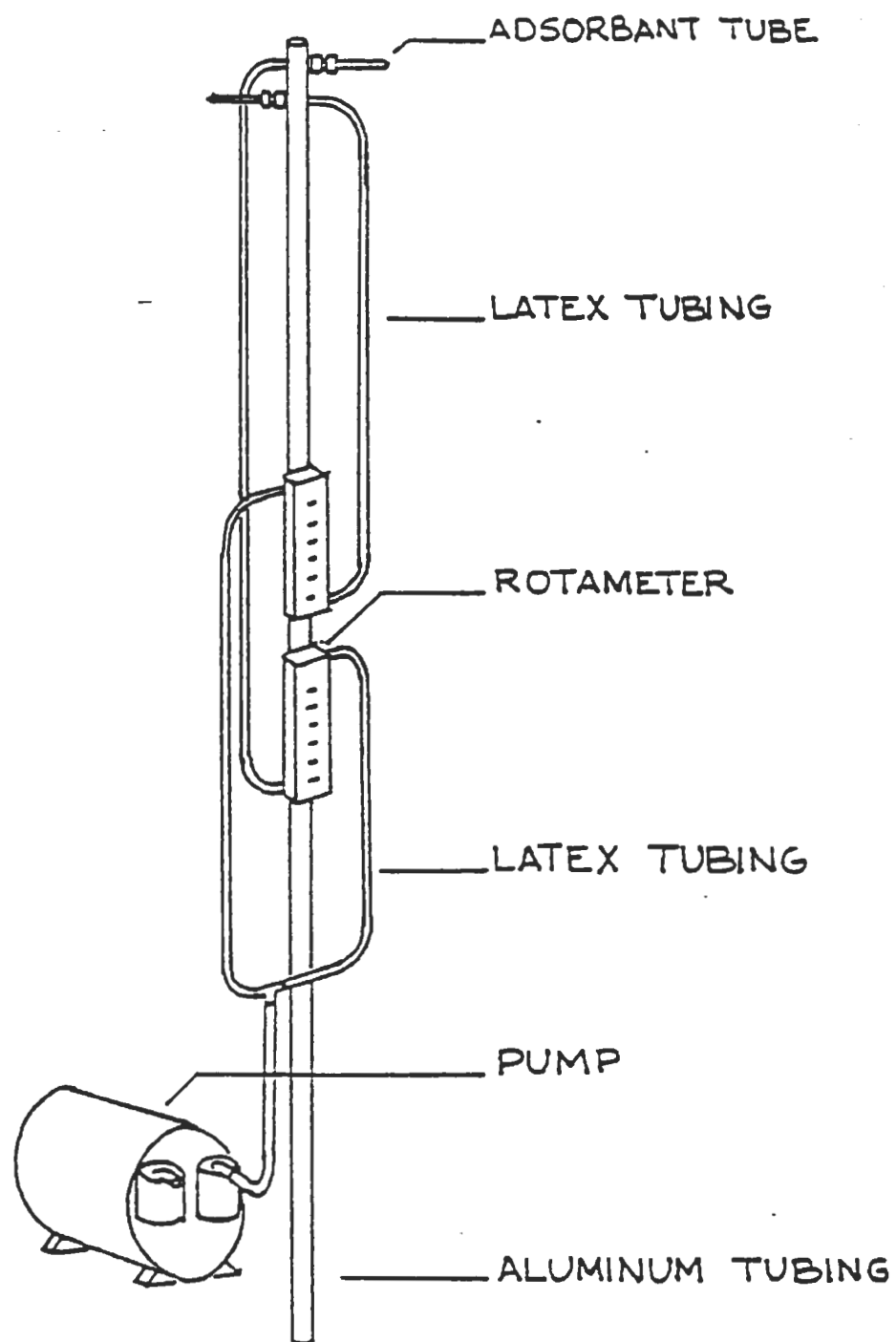


Figure 1. Air Sampler used in the monitoring of Methidathion and Methidaoxon

Table 2. Results of the flow rate audit of the ERI samplers.

<u>Site</u>	<u>Rotameter Number</u>	<u>Reported Flow (lpm)</u>	<u>True Flow (lpm)</u>	<u>Percent Difference</u>
Visalia - ARB	9	3.45	3.47	-0.6
	10	3.47	3.42	1.5
Exeter High School	5	3.45	3.48	-0.9
	6	3.43	3.42	0.3
U.C. Field Station	7	3.44	3.47	-0.9
	8	3.45	3.44	0.3
Jefferson Elementary School	11	3.44	3.33	3.3
	12	3.49	3.37	3.6
Sunnyside Union Elementary School	1	3.49	3.35	4.2
	2	3.47	3.38	2.7

Table 3. Results of the pre-application flow rate audit of the EEB samplers.

<u>Sampler Number</u>	<u>Rotameter Number</u>	<u>Reported Flow (lpm)</u>	<u>True Flow (lpm)</u>	<u>Percent Difference</u>
5	10	1.85	1.82	1.6
	11	1.86	1.86	0.0
7	13	1.87	1.86	0.5
	14	1.88	1.82	3.3
9	3B	1.85	1.82	1.6
	17	1.85	1.79	3.4

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

Table 4. Results of the post-application flow rate audit of the EEB samplers.

<u>Sampler Number</u>	<u>Rotameter Number</u>	<u>Reported Flow (lpm)</u>	<u>True Flow (lpm)</u>	<u>Percent Difference</u>
5	10	1.85	1.82	1.6
	11	1.86	1.82	2.2
7	13	1.87	1.83	2.2
	14	1.88	1.83	2.7
9	38	1.85	1.83	1.1
	17	1.85	1.84	0.5

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

LABORATORY AUDIT

A system audit of the Engineering Research Institute's laboratory operations in support of the Methidathion and Methidaoxon monitoring project was conducted between July 10, 1991 and June 8, 1992, by Gabriel Ruiz. The audit was conducted primarily through electronic mail and telephone conversations with Brenda Royce of the ERI, and it consisted of a review of the instrumentation, a review of the quality control measures used to monitor data quality, and an analytical performance audit. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected every 24-hours, stored inside individual screw cap glass culture tubes in an ice chest, and delivered to the laboratory on a daily basis. The samples were stored in a freezer at -10 to -15°C and extracted within one week. The extracts were then stored in the freezer, and analyses were performed within one month. The unused part of the extracts was retained until the end of the study.

Laboratory Instrumentation

Analysis of the samples was performed with a Varian 3400 Gas Chromatograph equipped with an electron capture detector. The chromatograph was interfaced to a Varian 4290 integrator. The integrator was used for area counts only, and the concentrations were determined by separate calculations.

Sample Analysis

The analytical procedure was developed by the ERI's laboratory staff and documented in a preliminary draft entitled "Standard Operating Procedure for the Determination of Methidathion and Methidaoxon in Ambient Air". The method entails extraction with toluene followed by GC analysis. (Refer to the draft of the SOP available in the QA office for further details.)

The detection limit of the method was determined as 0.05 ug total mass for Methidathion and 0.13 ug for Methidaoxon, using three standard deviations at the lowest calibration point plus the absolute value of the intercept. Since the detector had a non-linear calibration curve, a second-order best fit curve of area count vs. concentration was used to determine the concentrations.

The method recovery rates averaged 106% for Methidathion samples ranging in size from 0.06 to 1.6 ug, and 126% for Methidaoxon samples ranging in size from 0.3 ug to 3.0 ug. A retention efficiency study was conducted for triplicate samples containing 0.3 ug Methidathion and 1.5 ug Methidaoxon. After drawing ambient air through the tubes at 4 lpm for 24-hours, the average recoveries were 89% for Methidathion and 108% for Methidaoxon. Sample stability data was not reported to the Quality Assurance Section.

Quality control activities performed routinely to monitor and document the data quality included the following: daily four-point calibration, a calibration update every 10 samples, analysis of one control sample per batch of field samples, plotting of control charts with control limits defined at ± 3 standard deviations, analysis of a field duplicate per sampling day, replicate analyses of 5% of the samples, analysis of a lab and field spike every 10 samples, and analysis of a lab blank for every batch of samples. In addition, field blanks were analyzed occasionally, and qualitative confirmations were made with a Hall electrolytic conductivity detector.

Documentation

The ERI's laboratory staff followed adequate chain-of-custody procedures. All samples were accompanied by field data sheets and chain-of-custody records. A unique laboratory sample number independent of the field sample number was assigned to each sample when it was logged in. In addition, the extracts were given a separate laboratory number, and all the numbers were cross-referenced.

Sample logs, laboratory records, and instrument run and maintenance logs were kept in bound notebooks with numbered pages. The entries included sample number, sample type, date sample was received, date of analysis, raw analytical data, results of the analysis, and receptor of the analytical data.

The chromatograms, integrator printouts, and summary sheets for the analysis sequence were saved in an accessible form. Data reduction and calculations were performed on an electronic spreadsheet and the finalized data were stored on electronic media.

Analytical Performance Audit

The performance of the ERI's analytical method was evaluated by submitting for analysis a set of six audit samples spiked with measured amounts of Methidathion and Methidaoxon. The samples were prepared by Gabriel Ruiz on July 30, 1991, following the procedures outlined in Attachment II. The samples were analyzed on August 2, following the laboratory's standard operating procedures.

The analytical results for Methidathion showed a positive bias averaging 16.7% and ranging from 11.5% to 23.1% (Table 5). The results for duplicate samples M2 and M3 indicate a high degree of precision, but it also must be noted that sample M6 was reported as nondetectable, even though it was spiked with more than twice the detection limit value for Methidathion.

The Methidaoxon results showed more variability (Table 6). The difference between the assigned and the reported values averaged 16.5% and ranged from -1.2% to 42.9%. The results for duplicate samples M2 and M6 also indicate a high degree of precision for the method. Samples M4 and M5 were not spiked with Methidaoxon, but the laboratory reported masses of 0.28 and 0.18 ug per sample, respectively.

CONCLUSIONS

The ERI followed good quality control procedures overall. The sampling was conducted following good practices, sample handling and storage were appropriate, the analytical method was validated, and the documentation was adequate. The analytical audit results showed a fair agreement between the assigned and the reported mass of both compounds and were consistent with the method's recovery rates.

The only area that we feel needs further attention is the possibility of interference. The reported method recovery rates were greater than 100% for both compounds in most studies, and the audit results confirmed them. Moreover, the laboratory reported positive results for two Methidaoxon blanks (although breakdown of Methidathion could have accounted for the positive reading in one of the samples, the other was a blank for both compounds). Further analyses of the method validation and quality control data may be necessary to characterize the magnitude and possible source of the interference.

Table 5. Results of ERI's analyses of Methidathion audit samples.

<u>Sample ID</u>	<u>Assigned Mass (ug)</u>	<u>Reported Mass (ug)</u>	<u>Percent Difference</u>
M1	0	ND	N/A
M2	0.26	0.32	23.1
M3	0.26	0.30	15.4
M4	0	ND	N/A
M5	0.52	0.58	11.5
M6	0.13	ND	N/A

Table 6. Results of ERI's analyses of Methidaoxon audit samples.

<u>Sample ID</u>	<u>Assigned Mass (ug)</u>	<u>Reported Mass (ug)</u>	<u>Percent Difference</u>
M1	1.68	1.97	17.3
M2	0.84	0.83	- 1.2
M3	0.42	0.60	42.9
M4	0	0.28	N/A
M5	0	0.18	N/A
M6	0.84	0.90	7.1

ND = Not Detected

Percent Difference = $\frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$

Flow Audit Procedure for Pesticide Samplers

Introduction

The pesticide sampler is audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable primary standard gas flow calibration system.

The audit device is placed in series with the sample probe inlet and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's reported flow rate is then compared to the true flow rate, and a percent difference is determined.

Equipment

The basic equipment required for the pesticide sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fitting.
6. 1/4" I.D. Tygon tubing.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the teflon tubing to the outlet port of the audit device with the Swagelock fitting.
3. Connect the free end of the teflon tubing to the sampler probe inlet with a small section of Tygon tubing.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the reported flow rate.

Performance Audit Procedure
For The Laboratory Analysis Of Methidathion

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Methidathion and its breakdown product Methidaoxon. The audit is conducted by submitting audit samples prepared by spiking XAD-2 resin tubes with measured amounts of Methidathion and Methidaoxon. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Methidathion, neat compound
2. Methidaoxon, neat compound
3. Toluene, high purity
4. XAD-2 Resin Tubes
5. 50 ul Microsyringe

Safety Precautions

Methidathion and Methidaoxon may be fatal if inhaled, swallowed, or absorbed through the skin. Avoid direct physical contact. Vapors or direct eye contact can cause severe eye burns. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

3 mg/ml Methidathion Stock Solution: Weigh about 30 mg of Methidathion into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

4 mg/ml Methidaoxon Stock Solution: Weigh about 40 mg of Methidaoxon into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

12 ug/ml Methidathion Spiking Standard: Transfer 100 ul of the 3 mg/ml Methidathion stock solution to a clean 25 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

40 ug/ml Methidaoxon Spiking Standard: Transfer 100 ul of the 4 mg/ml Methidaoxon stock solution to a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

Sample Preparation

Prepare six audit samples from the Methidathion and Methidaoxon spiking standards according to the following table:

<u>Sample</u>	<u>Methidathion</u> <u>12 ug/ml Std</u>	<u>Methidaoxon</u> <u>40 ug/ml Std</u>
1	10 ul	20 ul
2	20	20
3	20	10
4	40	0
5	0	40
6	0	0

1. Break off the inlet end of the sample tube.
2. Insert the syringe needle into the adsorbant bed of the primary section of the tube, and slowly inject the appropriate volume of spiking solution. Do not allow the liquid to run down the sides of the tube.
3. Cap the open end of the tube with the plastic cap provided.
4. Assign a random number to each sample, keeping track of the concentrations. Label each tube with its assigned number and store at or below 4°C until ready for analysis.

APPENDIX F

METHOD VALIDATION RESULTS

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF ug	METHIDAOXON		FORTIF. ug	METHIDATHION	
		RESULTS ug	RECOV. %		RESULTS ug	RECOV. %
EXTRACTION EFFICIENCY						
Level 1	0.30	0.435	144.9%	0.06	0.061	102.0%
		0.511	170.2%		0.082	136.0%
		0.391	130.2%		0.055	91.0%
	Average:		148.4%			109.7%
	Std Dev:		20.2%			23.5%
Level 2	1.5	1.882	125.5%	0.3	0.316	105.2%
		1.464	97.6%		0.245	81.8%
		2.013	134.2%		0.284	94.6%
		1.574	104.9%		0.331	110.4%
		1.737	115.8%		0.330	110.2%
	Average:		115.6%			100.4%
	Std Dev:		14.8%			12.2%
Level 3	3.0	2.832	94.4%	0.6	0.774	129.0%
		3.327	110.9%		0.748	124.7%
		2.805	93.5%		7.684	114.0%
	Average:		99.6%			122.6%
	Std Dev:		9.8%			7.7%
Level 4	10.9	13.52	124.0%	9.8	10.26	104.8%
INJECTION REPRODUCIBILITY						
Level 1	0.3	0.391		0.06	0.052	
		0.396			0.055	
		0.380			0.070	
	Average:	0.389			0.059	
	Std Dev:	0.0078			0.0098	
	Rel SD:	2.00%			16.57%	
Level 2	1.5	2.013		0.3	0.284	
		1.670			0.300	
		2.324			0.311	
	Average:	2.002			0.298	
	Std Dev:	0.327			0.0135	
	Rel SD:	16.4%			4.51%	

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF.	METHIDAOXON		FORTIF.	METHIDATHION	
	<u>ug</u>	RESULTS <u>ug</u>	RECOV. <u>%</u>	<u>ug</u>	RESULTS <u>ug</u>	RECOV. <u>%</u>
INJECTION REPRODUCIBILITY (cont'd)						
Level 3	3.0	2.805 2.484 2.670		0.6	0.834 0.744 0.816	
		Average: 2.653			0.798	
		Std Dev: 0.161			0.0476	
		Rel SD: 6.08%			5.97%	
RETENTION EFFICIENCY						
Blank	0.0	0.150 0.142	— —	0.0	0.012 0.007	— —
Level 1	0.3	0.353 0.279 0.326	117.6% 93.0% 108.8%	0.06	0.078 0.090 0.110	130.5% 150.5% 183.5%
		Average:	106.5%			154.8%
		Std Dev:	11.8%			25.2%
Level 2	1.5	1.639 1.558 1.444 1.723	109.3% 103.9% 96.3% 114.9%	0.3	0.399 0.369 0.253 0.269	133.0% 123.0% 84.2% 89.7%
		Average:	106.1%			107.8%
		Std Dev:	7.9%			24.2%
Level 3	3.0	3.125 3.005 3.204	104.2% 100.2% 106.8%	0.6	0.589 0.645 0.619	98.2% 107.5% 103.2%
		Average:	103.7%			102.9%
		Std Dev:	3.2%			4.4%
Level 4	54.5	61.38	112.6%	49.0	62.69	128.1%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF.	METHIDATHION RESULTS	RECOV.	FORTIF.	METHIDATHION RESULTS	RECOV.
	<u>ug</u>	<u>ug</u>	<u>%</u>	<u>ug</u>	<u>ug</u>	<u>%</u>
RETENTION BREAKTHROUGH - BACK UP SECTION						
Level 1	10.9	0.126 0.150	1.2% 1.4%	9.8	ND ND	— —
Level 2	27.3	0.097	0.4%	24.5	ND	—
Level 3	54.5	0.126 0.148	0.2% 0.3%	49.0	ND ND	— —
Level 4	109.0	0.140	0.1%	97.9	ND	—
STORAGE STABILITY						
Freezer Stability						
03 Day	1.5	1.193 1.370 1.514	79.5% 91.3% 100.9%	0.3	0.431 0.486 0.485	143.8% 161.9% 161.5%
	Average:		90.6%			155.7%
	Std Dev:		10.7%			10.3%
07 Day	1.5	1.968 1.768 1.936	131.2% 117.9% 129.1%	0.3	0.427 0.305 1.384	142.4% 101.6% 128.0%
	Average:		126.1%			124.0%
	Std Dev:		7.2%			12.8%
14 Day	1.5	1.728 1.540 1.534	115.2% 102.6% 102.3%	0.3	0.369 0.350 0.295	123.0% 116.8% 98.4%
	Average:		106.7%			112.7%
	Std Dev:		7.4%			12.8%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF.	METHIDAOXON RESULTS	RECOV.	FORTIF.	METHIDATHION RESULTS	RECOV.
	<u>ug</u>	<u>ug</u>	<u>%</u>	<u>ug</u>	<u>ug</u>	<u>%</u>
STORAGE STABILITY						
Freezer Stability (cont'd)						
21 Day	1.5	1.848	123.2%	0.3	0.376	125.2%
		2.130	142.0%		0.367	122.4%
		2.157	143.8%		0.353	117.7%
			136.3%			121.8%
			11.4%			3.8%
28 Day	1.5	2.075	138.4%	0.3	0.332	110.7%
		1.663	110.9%		0.317	105.6%
		1.694	112.9%		0.285	95.1%
			120.7%			103.8%
			15.3%			8.0%
80 Day	1.5	1.3353	89.0%	0.3	0.274	91.2%
Ice Chest Stability						
01 Day	1.5	1.603	106.9%	0.3	0.259	86.2%
		1.967	131.1%		0.310	103.3%
		1.740	116.0%		0.375	125.1%
			118.0%			104.9%
			12.2%			19.5%
03 Day	1.5	2.353	156.8%	0.3	0.370	123.2%
		2.345	156.3%		0.393	131.1%
		1.196	79.7%		0.392	130.9%
			131.0%			128.4%
			44.4%			4.5%
07 Day	1.5	1.853	123.5%	0.3	0.371	123.6%
		1.781	118.8%		0.368	122.6%
		1.983	132.2%		0.329	109.8%
			124.8%			118.7%
			6.8%			7.7%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF.	METHIDAOXON		FORTIF.	METHIDATHION	
	<u>ug</u>	<u>RESULTS</u> <u>ug</u>	<u>RECOV.</u> <u>%</u>	<u>ug</u>	<u>RESULTS</u> <u>ug</u>	<u>RECOV.</u> <u>%</u>
STORAGE STABILITY						
Room Temperature Stability						
01 Day	1.5	2.336	155.7%	0.3	0.259	862%
		1.868	124.5%		0.310	1033%
			140.1%			948%
			22.1%			121%
03 Day	1.5	1.600	106.6%	0.3	0.323	1077%
		1.513	100.9%		0.348	1160%
			103.8%			1119%
			7.1%			58%
07 Day	1.5	1.139	75.9%	0.3	0.230	767%
		1.855	123.7%		0.336	1121%
			99.8%			944%
			33.7%			250%
FIELD CONTROLS						
Blank	0.0	0.161	—	0.0	0.008	—
		0.107	—		0.010	—
		0.114	—		0.007	—
Spike	1.5	1.759	117.3%	0.3	0.324	1080%
		1.642	109.5%		0.361	1203%
		1.811	120.7%		0.335	1117%
			115.8%			1133%
			5.7%			63%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF.	METHIDAOXON		FORTIF.	METHIDATHION	
	<u>ug</u>	RESULTS <u>ug</u>	RECOV. <u>%</u>	<u>ug</u>	RESULTS <u>ug</u>	RECOV. <u>%</u>
EXTRACTION CONTROLS						
	1.5	2.222	148.1%	0.3	0.392	130.8%
	1.5	1.400	93.3%	0.3	0.457	152.2%
	1.5	1.861	124.1%	0.3	0.325	108.3%
	1.5	1.785	119.0%	0.3	0.359	119.8%
	1.5	2.510	167.3%	0.3	0.311	103.5%
	1.5	1.986	132.4%	0.3	0.419	139.8%
	1.5	2.348	156.5%	0.3	0.445	148.4%

Control Limits:

UCL	3.064	0.589
UWL	2.852	0.523
LWL	1.004	0.259
LCL	0.592	0.194